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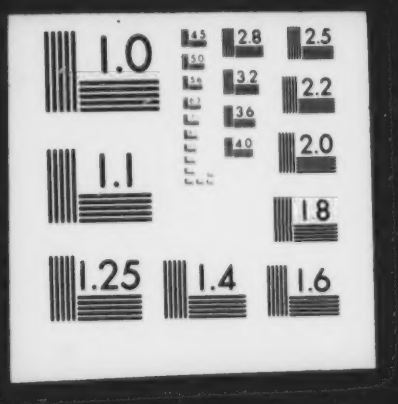

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MATHEMATICAL SIMULATION OF AN ADSORBER FOR POLLUTANT REMOVAL

KANSAS STATE UNIVERSITY

PREPARED FOR
NATIONAL ENVIRONMENTAL RESEARCH CENTER

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16. ABSTRACT The first portion of the report: comprehensively surveys the literature on design and operational aspects of processes for adsorbing gaseous pollutants; and summarizes mathematical models of these processes. The second portion of the report: presents mathematical models (based on the mechanism of external mass transfer rate control and a Langmuir type isotherm) for the adiabatic adsorption processes in a fixed bed of adsorbent, taking into account axial dispersion of the pollutant; presents the transient solution (obtained by solving numerically the governing equations using the Crank-Nicolson implicit method) for the dynamic adsorbate concentrations and temperature at various bed positions; and presents results of studies on the effects of various parameters. The third portion of the report: describes a single fixed-bed pollutant adsorber operated cyclically by synchronizing the change in direction of the gaseous flow with the change in temperature; presents two operational schemes for such a system; and discusses effects of several parameters on adsorber performance.

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1. INTRODUCTION

The adsorption process has been employed mostly in the separation of fluids and solvent recovery. Increasingly the adsorption process is being employed for pollutant removal from air. In the first section of this report, a comprehensive survey of the literature on design and operational aspects of processes for adsorbing gaseous pollutants is given. Mathematical models of these processes are also summarized. In the second section of this report, mathematical models for the adiabatic adsorption processes in a fixed bed of adsorbent are presented. The models take into account axial dispersion of the pollutant and are based on the mechanisms of external mass transfer rate control and a Langmuir type isotherm. The transient solution is presented for the dynamic adsorbate concentrations and temperature at various positions of the bed. The solution was obtained by solving numerically the governing equations using the Crank-Nicolson implicit method. Results of the studies on the effects of various parameters are also presented. The third section of this report, describes a single fixed bed pollutant adsorber operated cyclically by synchronizing the change in the direction of the gaseous flow with the change in temperature. Two operational schemes are presented for such a system. Effects of several parameters on the adsorber performance are discussed.

2. LITERATURE SURVEY AND MATHEMATICAL MODELING

A packed bed adsorber can be used for controlling gaseous pollutants (Hirschler and Amon, 1947; Mair et al., 1947; Lorentz, 1950; Turk and Bownes, 1951; Turk, 1968; Lippmaa and Luiga, 1970; Mattia, 1970; Turk, 1970; Turk et al., 1972). This report presents a comprehensive survey of the literature on design and operational aspects of gas adsorbers which are employed for controlling obnoxious substances emitted from stationary sources such as restaurants, auto repair or paint shops, gasoline storage and transfer areas, dry cleaning shops, industrial factories, and process plants. Although the pollutant emission from any of such sources may often be negligible in quantity, the pollutants (mostly aromatic hydrocarbons) have objectionable properties such as odor or toxicity (Patty, 1942; Hayashi and Hayashi, 1969). In addition, there is a large number of such sources and, therefore, the overall contribution of these sources to air pollution is significant. Available and plausible "operational" mathematical models of the adsorbers are also summarized in this report.

An adsorption unit which consists of two fixed bed columns of adsorbent is considered in this section. In the cycle of operation, one of the columns is always in the regeneration mode and the other is in the adsorption mode. Activated carbon is most frequently employed as the adsorbent since it is commercially available in quantity and adsorbs essentially all types of organic gases and vapors regardless of variation in concentration and humidity. The recently invented doped active carbons (Inagaki, 1970) and sieving active carbons (Kawazoe et al., 1971; Takeuchi et al., 1972) can also be employed.

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A mathematical model for a fixed adsorption bed should take into account, at least, the dynamic changes of the adsorbate concentrations in both the gaseous and solid phases at various positions in the bed. Some published papers on modeling the adsorption processes in fixed beds (Vermeulen, 1958; Masamune and Smith, 1964; Carter, 1966; Meyer and Weber, 1967; Schneider and Smith, 1968; Lee and Weber, 1969a, 1969b; Chu and Tsang, 1971; Gariepy and Zwiebel, 1971; Thomas and Lombardi, 1971; Carter and Husain, 1972; Cooney and Shieh, 1972; Cooney and Strusi, 1972; Gupta and Greenkorn, 1972; Tada et al., 1972b) are available. Modeling of the concentration dynamics can usually be accomplished either by taking a mass balance (for an isothermal process) or by taking mass and energy balances (for a nonisothermal process) over a control volume of the bed. Interphase mass or heat transport is often considered to be the rate controlling mechanism (Geser and Canjar, 1962; Carter, 1966; Meyer and Weber, 1967; Hiraoka et al., 1968; Rimpel et al., 1968; Schneider and Smith, 1968; Lee and Weber, 1969a, 1969b; Masamune and Smith, 1969; Gariepy and Zwiebel, 1971; Thomas and Lombardi, 1971; Carter and Husain, 1972; Cooney and Shieh, 1972; Cooney and Strusi, 1972; Ikeda et al., 1972).

Since the rate of interphase mass transfer depends on the degree of saturation of adsorbate on adsorbent, knowledge of the equilibrium state is required in modeling it. Mathematical models for the various types of equilibrium states have been delineated (Brunauer, 1943; Young and Crowell, 1962). Experimental equilibrium data, specifically those for the adsorption of gaseous hydrocarbons on activated carbon, and the various adsorption equilibrium models to represent such data are available (Brunauer et al., 1938; Lewis et al., 1950; Kapfer et al., 1956; Geser and Canjar, 1962; Grant et al., 1962; Cook and Basmadjian,

1964; Grant and Manes, 1964; Meyer and Weber, 1967; Lee and Weber, 1969b; Clapham et al., 1970; McCarthy, 1971; Thomas and Lombardi, 1971).

A mathematical model for regeneration of deactivated adsorbent is also necessary in developing the optimum design and operating procedure of an adsorption system since the system includes both adsorption and regeneration steps in its cyclic operation. The regeneration of deactivated adsorbent is usually carried out by raising the temperature of the adsorbent. For example, the regeneration of deactivated carbon is accomplished by passing saturated steam at low pressure countercurrently through the carbon bed. Although the regeneration process is often referred to as a reverse process of adsorption, experimental data as well as theoretical analysis to support this hypothesis are meager. It has been reported, however, that there is no indication of the existence of a hysteresis phenomenon in adsorption and desorption (Lewis et al., 1950).

To predict the adsorbate concentration change in the bed with respect to time, the mass balance or the mass and energy balances given in the form of differential equations must be solved either analytically or numerically. For the case of simple linear differential equation the analytical solution can be obtained (Bohart and Adams, 1920; Thomas, 1944; Hiester and Vermeulen, 1952; Masamune and Smith, 1964; Gupta and Greenkorn, 1972). The governing equations are usually nonlinear differential equations. Furthermore, if the adsorption unit is operated nonisothermally, the governing equations are two coupled nonlinear partial differential equations. For these cases, the analytical solutions may not be available; however, various numerical methods can be used for the solution (Rosen, 1954; Lapidus, 1962; Liu and Amundson, 1962; Smith, 1965; Rosenbrock and Storey, 1966; Villadsen and Stewart, 1967; Finlayson, 1969; Forsythe and Wasow, 1969; Liu, 1969; Stewart, 1969; Chu and Tsang, 1971; Tada et al., 1972a).

2.1. MODELS OF ADSORPTION STEP

The mathematical expression for the rate of adsorption can be derived based on the known and/or postulated transport mechanism of the adsorbate. Such mechanism is often considered to consist of the following possible sequence of steps: (a) transport of adsorbate from the bulk of the fluid to the external surface of the adsorbent, (b) transport from the external surface into the interior surface of the adsorbent, and (c) adsorption on the adsorbent surface. Although each step offers resistance to adsorbate transport, a single rate controlling step is often considered to provide the major portion of the overall resistance. There can be, therefore, three types of rate controlling models, each of them giving a different form of the rate expression for adsorption.

(a) External mass transfer controlling

$$R_a = k_e \rho_g a(c - c^*) \tag{1}$$

(b) Intraparticle diffusion controlling

$$R_a = D_i a \rho_g \left(\frac{\partial c_i}{\partial r}\right)_{r=r_0} \tag{2}$$

where $\left(\frac{\partial c_i}{\partial r}\right)_{r=r_0}$ is determined by solving the differential equation

$$\rho_g D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r}\frac{\partial c_i}{\partial r}\right) = H_g \frac{\partial c_i}{\partial t} + H_s \frac{\partial q}{\partial t} \tag{3}$$

with initial and boundary conditions

$$\begin{aligned} &\text{when } t = 0, && c_i = 0 \\ &\text{at } r = 0, && \frac{\partial c_i}{\partial r} = 0 \end{aligned} \tag{4}$$

at $r = r_0$, $\quad c_i = c(z, t)$

(c) Surface adsorption controlling

$$R_a = k_a \, Sc \, \rho_g \left(1 - \frac{q}{q^\infty}\right) - k_d \, S \, \frac{q}{q^\infty} \qquad (5)$$

Notations employed in these equations are defined as follows:

R_a = overall rate of adsorption per unit volume of bed, g/sec-cm^3

k_e = external mass transfer coefficient based on external surface of particle and concentration driving force, cm/sec

a = available external surface area per unit volume of bed, cm^2/cm^3

c = mass fraction of adsorbate in the bulk fluid, g of adsorbate/g of adsorbate free gas

c_i = mass fraction of adsorbate of the fluid in the particle, g of adsorbate/g of adsorbate free gas

H_g = gas phase hold-up, i.e., mass of gas per unit volume of bed, g of gas/cm^3 of bed

H_s = solid phase hold-up, i.e., mass of adsorbent per unit volume of bed, g of adsorbent/cm^3 of bed

D_i = effective intraparticle diffusivity, cm^2/sec

c^* = equilibrium composition, g of adsorbate/g of adsorbate free gas

r = radial distance from center of spherical particle, cm

r_0 = radius of spherical particle, cm

ρ_g = density of gas, g/cm^3

t = time, sec

q^∞ = maximum amount of adsorbate which can be adsorbed per unit mass of adsorbent, g of adsorbate/g of adsorbent

q = amount of adsorbate adsorbed per unit mass of adsorbent, g of adsorbate/g of adsorbent

z = axial distance from entrance of bed, cm

k_a = adsorption rate constant per unit surface area of pores, cm/sec

S = pore surface area per unit volume of bed, cm^2/cm^3

k_d = desorption rate constant per unit surface area of pores, $g/sec\text{-}cm^2$

Since the adsorption rate depends on the degree of saturation of adsorbate on adsorbent, a mathematical model for the equilibrium state is necessary to express the rate equation explicitly. A variety of mathematical expressions based on various adsorption theories such as Langmuir's monolayer theory (Langmuir, 1918, 1932; Brunauer, 1943; Suits, 1961; Young and Crowell, 1962), Freundlich's equation (Freundlich, 1922; Brunauer, 1943), Polanyi's potential theory (Brunauer, 1943; Young and Crowell, 1962), the capillary condensation theory (McGavack and Patrick, 1920; Brunauer, 1943), and the BET equation (Brunauer et al., 1938; Brunauer et al., 1940; Brunauer, 1943; Young and Crowell, 1962) are available. For example, the BET equation based on the finite multilayer theory can be written in terms of vapor pressure as

$$q = \frac{q^{\infty} b_1 \left(\frac{p}{p_0}\right)}{1 - \frac{p}{p_0}} \left[\frac{1 - (n+1)\left(\frac{p}{p_0}\right)^n + n\left(\frac{p}{p_0}\right)^{n+1}}{1 + (b_1 - 1)\left(\frac{p}{p_0}\right) - b_1\left(\frac{p}{p_0}\right)^{n+1}} \right] \qquad (6)$$

$$b_1 = e^{(\Delta H_a - \Delta H_c)/RT} \qquad (7)$$

where

p = vapor pressure, mm Hg or psi

p_0 = saturated vapor pressure at temperature T, mm Hg or psi

n = number of layers

ΔH_a = heat of adsorption, cal/g-mole

ΔH_c = heat of condensation, cal/g-mole

R = gas constant, cal/g-mole-°K

T = temperature, °K

The BET equation, equation (6), becomes identical to the expression of Langmuir's monolayer theory (Type I isotherm), if $n = 1$. If $n > 1$, either Type II or Type III isotherm is obtained, depending on the value of constant b_1.

Regeneration Rate Equation: The rate expression for the regeneration step should be similar to the rate equation for the adsorption step with the exception that directions of adsorbate transport in the two steps are opposite. The identical equilibrium equation can also be employed since there is no indication of the existence of a hysteresis phenomenon associated with the adsorption-desorption cycle (Lewis et al., 1950).

2.2. FLOW MODELS

It is very difficult to represent mathematically the precise flow behavior of the fluid as it passes through the adsorption bed. However, based on some simplifying assumptions, the flow pattern in the bed may be approximated by different flow models, for example, the back-mix (completely mixed) flow model, plug flow model, and nonideal flow models such as the dispersion model, the compartment model, and the combined or mixed model (Levenspiel, 1962; Wen and Fan, 1974). The back-mix model (Levenspiel, 1962; Denbigh, 1966; Wen and Fan, 1974) assumes that the adsorbate concentration of the fluid is uniform throughout the bed. The governing equations for the model may be written as

$$H_g \frac{dc}{ct} = \frac{\rho_g}{\tau} (c_0 - c) + R_a \tag{8}$$

$$H_s \frac{dq}{dt} = R_a \tag{8a}$$

with initial conditions

$$c = q = 0 \qquad \text{when } t = 0 \tag{9}$$

where τ is the mean residence time based on the mass flow rate and c_0 is the inlet adsorbate concentration. This model is an oversimplified model for the flow through a fixed bed. It may serve, however, as a very rough approximation of the flow under certain circumstances where the effect of mixing is more significant than that of the overall convective motion in the bed. It may also serve as one of the two limiting or ideal cases which bound the actual flow behavior.

If the overall convective motion affects predominantly the movement of adsorbate, the plug flow model (Levenspiel, 1962; Denbigh, 1966;

Wen and Fan, 1974) approximates the flow better. The plug flow model (also called the piston flow model) assumes that no mixing of adsorbate is induced among elements of the fluid at different positions along the direction of flow; that is to say, the fluid is assumed to move through the adsorption bed like a plug. The governing equations for the model may be written as

$$H_g \frac{\partial c}{\partial t} = - G \frac{\partial c}{\partial z} - R_a \tag{10}$$

$$H_s \frac{\partial q}{\partial t} = R_a \tag{11}$$

with initial and boundary conditions

$$\text{when } t = 0, \qquad c = q = 0 \tag{12}$$

$$\text{at } z = 0, \qquad c = c_0 \tag{13}$$

where G is the superficial mass flow rate of fluid (g of gas/sec-cm^2). In practice, this model is more frequently used than any other in modeling a packed bed (Masamune and Smith, 1964; Carter, 1966; Meyer and Weber, 1967; Rimpel et al., 1968; Lee and Weber, 1969a, 1969b; Gariepy and Zwiebel, 1971; Thomas and Lombardi, 1971; Carter and Husain, 1972; Cooney and Shieh, 1972). This model also serves as a limiting or an ideal case which bounds the actual flow.

The actual flow pattern is neither a back-mix flow nor a plug flow. Therefore, the use of one of many available nonideal flow models that take into account the effect of axial and/or radial dispersion is desirable. If the (axial) dispersion model (Levenspiel, 1962; Denbigh, 1966; Wen and Fan, 1974) is employed, the governing equations are

$$H_g \frac{\partial c}{\partial t} = \phi \rho_g E_1 \frac{\partial^2 c}{\partial z^2} - G \frac{\partial c}{\partial z} - R_a \tag{14}$$

$$H_s \frac{\partial q}{\partial t} = R_a \tag{15}$$

with initial and boundary conditions

$$\text{when } t = 0, \qquad c = q = 0 \tag{16}$$

$$\text{at } z = 0, \qquad G(c)_{z=0^+} = Cc_0 + \phi \rho_g E_1 \left(\frac{\partial c}{\partial z}\right)_{z=0^+} \tag{17}$$

$$\text{at } z = L, \qquad \frac{\partial c}{\partial z} = 0 \tag{18}$$

where E_1 is the axial dispersion coefficient and ϕ is the void fraction of the bed. Here, the second boundary condition may not be rigorous since the condition at the exit of the finite bed is changing with respect to time for an unsteady state process. Since the time constant of concentration change at the exit is much larger than the length of the operating time, it may not be erroneous to use such a boundary condition. Some published papers employing this flow model are available (Schneider and Smith, 1968; Chu and Tsang, 1969; Cooney and Strusi, 1972; Gupta and Greenkorn, 1972; Ikeda et al., 1972).

Other nonideal flow models which are often employed to approximate the actual flow pattern through a fixed bed are the compartment model and the combined model (Levenspiel, 1962; Denbigh, 1966; Wen and Fan, 1974). The compartment model (also called the cell model) (Deans and Lapidus, 1960; Levenspiel, 1962; Wen and Fan, 1974) is based on a two-dimensional network of completely mixed tanks. If the radial concentration gradient in the fixed bed is negligibly small, the

two-dimensional network becomes a one-dimensional completely mixed tanks-in-series (with and without backflow). The governing equations for the model are derived from the input-output-accumulation analysis for all the cells. For the case of negligible radial concentration gradient, the compartment model is nearly equivalent to the axial dispersion model.

The combined model (also called the mixed model) assumes that the actual flow pattern is approximated by combinations of various ideal and nonideal flow models in parallel or in series or in mixed fashion. In addition, the model takes into account the effects of bypass flow, recycle flow and cross flow as well as dead space in the system. The governing equations for the model are obtained from the individual governing equations for the component systems and from the mode of combinations of the component systems with the bypass, recycle, and cross flows.

Isothermal and Nonisothermal Processes: Isothermal adsorption precludes heat effects; therefore, analysis can be based only on the material balance on adsorbate and the equilibrium relationship between adsorbate in the fluid and that in the adsorbent. The application is restricted to systems that have low inlet adsorbate concentration and high fluid velocity. This is also applicable to systems that have small heat of adsorption.

In practice, it is difficult to maintain strictly isothermal conditions since the adsorption process can be accompanied by considerable heat generation (Brunauer, 1943; Young and Crowell, 1962). The heat released in the adsorption process raises the temperature of the bed, and the rise in temperature decreases the adsorption rate. Therefore, analysis should include changes in energy as well as in the adsorbate

concentrations in both the body of the fluid and the adsorbent. For example, for the flow pattern represented by the dispersion model, the governing equations expressed in equations (14) through (18) should be accompanied by the energy balances

$$H_g c_g \frac{\partial T_g}{\partial t} = \phi E_2 \frac{\partial^2 T_g}{\partial z^2} - Gc_g \frac{\partial T_g}{\partial z} - h\, a(T_g - T_s) \quad (19)$$

$$H_s c_s \frac{\partial T_s}{\partial t} = (1 - \phi) E_3 \frac{\partial^2 T_s}{\partial z^2} + h\, a(T_g - T_s) + R_a(\Delta H) \quad (20)$$

The initial and boundary conditions are

$$\text{when } t = 0, \qquad T_g = T_s = T_0 \quad (21)$$

$$Gc_g (T_g)_{z=0^+} = Gc_g T_0 + \phi E_2 \left(\frac{\partial T_g}{\partial z}\right)_{z=0^+} \quad (22)$$

$$\text{at } z = 0, \qquad \frac{\partial T_s}{\partial z} = 0 \quad (22a)$$

$$\text{at } z = L, \qquad \frac{\partial T_g}{\partial z} = \frac{\partial T_s}{\partial z} = 0 \quad (23)$$

where

E_2 = thermal conductivity of gas in flow through the bed, cal/sec-°K-cm

h = heat transfer coefficient between gas and adsorbent, cal/°K-cm^2-sec

ρ_g = density of gas, g/cm^3

c_g = specific heat of gas, cal/°K-g

T_g = gas temperature, °K

T_s = solid temperature, °K

E_3 = thermal conductivity of solid, cal/sec-°K-cm

ρ_s = density of solid adsorbent, g/cm^3

c_s = specific heat of solid adsorbent, cal/°K-g

ΔH = average heat of adsorption, cal/g

T_0 = temperature at the inlet of the bed, °K

Recent noteworthy works on adsorption that have not been discussed so far are those by Ikeda et al. (1972), Tada et al. (1972a), Tada et al. (1972b).

Bohart, G. S. and E. Q. Adams, "Some Aspects of the Behavior of Charcoal with Respect to Chlorine," Am. Chem. Soc. J., 42, 523-544 (1920).

Brunauer, S., P. H. Emmett, and E. Teller, "Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc., 60, 309-319 (1938).

Brunauer, S., L. S. Deming, W. E. Deming, and E. Teller, "On a Theory of the Van der Waals Adsorption of Gases," J. Am. Chem. Soc., 62, 1723-1732 (1940).

Brunauer, S., "The Adsorption of Gases and Vapors, Volume I, Physical Adsorption," Princeton University Press, Princeton, N.J. (1943).

Carter, J. W., "A Numerical Method for Prediction of Adiabatic Adsorption in Fixed Beds," Trans. Instn. Chem. Engrs., 44, T253-T259 (1966).

Carter, J. W. and H. Husain, "Adsorption of Carbon Dioxide in Fixed Beds of Molecular Sieves," Trans. Instn. Chem. Engrs., 50, 69-75 (1972).

Chu, C. and L. C. Tsang, "Behavior of a Chromatographic Reactor," Ind. Eng. Chem. Process Des. Develop., 10, 47-53 (1971).

Clapham, T. M., T. J. Junker, and G. S. Tobias, "Activated Carbon Odorant Removal from Air Quantified," Prepared for presentation at the ASHRAE Annual Meeting, Kansas City, Mo., June 28 - July 1 (1970).

Cook, W. H. and D. Basmadjian, "Correlation of Adsorption Equilibria of Pure Gases on Activated Carbon," Can. J. Chem. Eng., 42, 146-151 (1964).

Cooney, D. O. and D. Shieh, "Fixed Bed Sorption with Recycle," AIChE Journal, 18, 245-247 (1972).

Cooney, D. O. and F. P. Strusi, "Analytical Description of Fixed-Bed Sorption of Two Langmuir Solutes Under Nonequilibrium Conditions," Ind. Eng. Chem. Fundam., 11, 123-126 (1972).

Deans, H. A. and L. Lapidus, "A Computational Model for Predicting and Correlating the Behavior of Fixed-Bed Reactors," AIChE Journal, 6, 656-663 (1960).

Denbigh, K., "Chemical Reactor Theory," Cambridge University Press, Cambridge, Mass. (1966).

Finlayson, B. A., "Applications of the Method of Weighted Residuals and Variational Methods," British Chem. Eng., 14, 53-57, 179-182 (1969).

Forsythe, G. E. and W. R. Wasow, "Finite-Difference Methods for Partial Differential Equations," AIChE Journal, 15, 334-338 (1969).

Freundlich, H., "Colloid and Capillary Chemistry," E. P. Dutton and Co. Inc., New York (1922).

Gariepy, R. L. and I. Zwiebel, "Adsorption of Binary Mixtures in Fixed Beds," a paper presented at the 68th National Meeting of the AIChE, Houston, Texas, Feb. 28 - March 4 (1971).

Geser, J. J. and L. N. Canjar, "Adsorption of Methan and Hydrogen on Packed Beds of Activated Carbon," AIChE Journal, 8, 494-497 (1962).

Grant, R. J., M. Manes, and S. B. Smith, "Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon," AIChE Journal, 8, 403-406 (1962).

Grant, R. J. and M. Manes, "Correlation of Some Gas Adsorption Data Extending to Low Pressures and Supercritical Temperatures," Ind. Eng. Chem. Fundamentals, 3, 221-224 (1964).

Gupta, S. P. and R. A. Greenkorn, "Dispersion During Flow in Porous Media with Adsorption," a paper presented at the 72nd National Meeting of the AIChE, St. Louis, Mo., May 21-24 (1972).

Hayashi, M. and S. Hayashi, "Nuisance Caused by Odor," Proceedings of The Osaka Prefectural Institute of Public Health, Edition of Industrial Health No. 7, September (1969).

Hiester, N. K. and T. Vermeulen, "Saturation Performance of Ion Exchange and Adsorption Columns," Chem. Eng. Prog., 48, 505-516 (1952).

Hiraoka, M., G. Matsuno, and T. Hanakawa, "A Consideration on the Mechanism of SO_2 Gas Adsorption on Activated Carbon," Air Conditioning and Sanitary Eng. (Japan), 42, 503-509 (1968).

Hirschler, A. E. and S. Amon, "Adsorption -- A tool in the preparation of high-purity saturated hydrocarbons," Ind. Eng. Chem., 39, 1585-1596 (1947).

Ikeda, K., O. Kanemitsu and K. Shimomura, "Fixed Bed Gas Adsorption under High Pressure," a paper presented at the 37th annual meeting of the Society of Chemical Engineers, Japan, Nagoya, Japan, April (1972).

Inagaki, K., "SO_2 Removal from Exhaust Gases by Adsorbents Catalyzed with Metallic Oxides," Aichi-Ken Kogyo Shidosho Report, Nogoya, Japan (1970).

Kapfer, W. H., M. Malow, J. Happel, and C. J. Marcel, "Fraction of Gas Mixtures in a Moving-bed Adsorber," AIChE Journal, 2, 456-467 (1956).

Kawazoe, K., V. A. Astakhov, T. Kawai, and Y. Eguchi, "Adsorption Equilibrium on Molecular-sieving Carbon," Kagaku Kogaku (Chemical Engineering, Japan), 35, 1006-1011 (1971).

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platimun," J. Am. Chem. Soc., 40, 1361-1403 (1918).

Langmuir, I., "Vapor Pressures, Evaporation, Condensation and Adsorption," J. Am. Chem. Soc., 54, 2798-2832 (1932).

Lapidus, L., "Digital Computation for Chemical Engineering," McGraw-Hill Co., New York (1962).

Lee, R. G. and T. W. Weber, "Isothermal Adsorption in Fixed Beds," Can. J. Chem. Eng., 47(1), 54-59 (1969a).

Lee, R. G. and T. W. Weber, "Interpretation of Methane Adsorption on Activated Carbon by Nonisothermal and Isothermal Calculations," Can. J. Chem. Eng., 47(1), 60-65 (1969b).

Levenspiel, O., "Chemical Reaction Engineering," John Wiley & Sons, New York (1962).

Lewis, W. K., E. R. Filliland, B. Chertow, and W. P. Cadogen, "Pure Gas Isotherms," Ind. Eng. Chem., 42, 1326-1332 (1950).

Lippmaa, E. T. and P. O. Luiga, "Concentration of Organic Air Contaminants by Sorbents," a paper presented at the 2nd International Clean Air Congress, Washington, D. C., Dec. 6-11 (1970).

Liu, S. L. and N. R. Amundson, "Stability of Adiabatic Packed Bed Reactors -- An Elementary Treatment," Ind. Eng. Chem. Fundamentals, 1, 200-208 (1962).

Liu, S. L., "Stable Explicit Difference Approximations to Parabolic Partial Differential Equations," AIChE Journal, 15, 334-338 (1969).

Lorentz, F., "Waste Disposal," Chem. Eng. Prog., 46(8), 377-379 (1950).

Mair, B. J., A. L. Gaboriault, and F. D. Rossini, "Assembly and Testing of 52-Foot Laboratory Adsorption Column -- Separation of hydrocarbons by adsorption," Ind. Eng. Chem., 39, 1072-1081 (1947).

Masamune, S. and J. M. Smith, "Adsorption Rate Studies -- Significance of Pore Diffusion," AIChE Journal, 10, 246-252 (1964).

Mattia, M. M., "Process for Solvent Pollution Control," Chem. Eng. Prog., 66(12), 74-79 (1970).

McCarthy, W. C., "Adsorption of Light Hydrocarbons from Nitrogen with Activated Carbon," Ind. Eng. Chem. Process Des. Develop., 10, 13-18 (1971).

McGavack, J., Jr. and W. A. Patrick, "The Adsorption of Sulfur Dioxide by the Gel of Silicic Acid," J. Am. Chem. Soc., 42, 946-978 (1920).

Meyer, O. A. and T. W. Weber, "Nonisothermal Adsorption in Fixed Beds," AIChE Journal, 13, 457-465 (1967).

Patty, F. A., editor, "Industrial Hygiene and Toxicology, Vol. II," Interscience Publishers, Inc., New York (1942).

Rimpel, A. E., Jr., D. T. Camp, J. A. Kostecki, and L. N. Canjar, "Kinetics of Physical Adsorption of Propane from Helium on Fixed Beds of Activated Alumina," AIChE Journal, 14, 19-24 (1968).

Rosen, J. B., "General Numerical Solution for Solid Diffusion in Fixed Beds," Ind. Eng. Chem., 46, 1590-1594 (1954).

Rosenbrock, H. H. and C. Storey, "Computational Techniques for Chemical Engineers," Pergamon Press, New York (1966).

Schneider, P. and J. M. Smith, "Adsorption Rate Constants from Chromatography," AIChE Journal, 14, 762-771 (1968).

Smith, G. D., "Numerical Solution of Partial Differential Equations," Oxford University Press, Oxford (1965).

Stewart, W. E., "Solution of Transport Problems by Collocation Methods," AIChE Continuous Education Series, No. 4, pp. 114-135 (1969).

Suits, C. G., editor, "The Collected Works of Irving Langmuir, Vol. 9, Surface Phenomena," Pergamon Press, New York (1961).

Tada, K., S. Shikagawa, and I. Nakamori, "Measurement of Adsorption Characteristics by Gas Chromatographic Method, (I)," a paper presented at the 37th annual meeting of the Society of Chemical Engineers, Japan, Nagoya, Japan, April (1972a).

Tada, K., S. Shikagawa, and I. Nakamori, "Measurement of Adsorption Characteristics by Gas Chromatographic Method, (II)," a paper presented at the 37th annual meeting of the Society of Chemical Engineers, Japan, Nagoya, Japan, April (1972b).

Takeuchi, T., E. Furutani, and Y. Eguchi, "Liquid Phase Adsorption Equilibrium on Molecular-sieving Carbon," a paper presented at the 37th annual meeting of the Society of Chemical Engineers, Japan, Nagoya, Japan, April (1972).

Thomas, H. C., "Heterogeneous Ion Exchange in a Flowing System," Am. Chem. Soc. J., 66, 1664-1666 (1944).

Thomas, W. J. and J. L. Lombardi, "Binary Adsorption of Benzene-Toluene Mixtures," Trans. Instn. Chem. Engrs., 49, 240-250 (1971).

Turk, A. and K. A. Bownes, "Adsorption Can Control Odors," Chem. Eng., 58(5), 156-158 (1951).

Turk, A., "Industrial Odor Control," Chem. Eng., 77(9), 199-206 (1970).

Turk, A., R. C. Haring, and R. W. Okey, "Odor Control Technology," Environmental Science and Technology, 6, 602-607 (1972).

Vermeulen, T., "Separation by Adsorption Methods," in Vol. II of Advances in Chemical Engineering Edited by T. B. Drew and J. W. Hoopes, Jr., Academic Press, New York (1958).

Villadsen, J. V. and W. E. Stewart, "Solution of Boundary-Value Problems by Orthogonal Collocation," Chem. Eng. Sci., 22, 1483-1501 (1967).

Wen, C. Y. and L. T. Fan, "Models for Flow Systems," Monograph to be published, Gordon and Breach, New York (1974).

Young, D. M. and A. D. Crowell, "Physical Adsorption of Gases," Butterworth, London (1962).

3. MODELING AND SIMULATION OF AN ADIABATIC ADSORBER PERFORMANCE

A packed bed adsorption unit appears to be one of the most practical devices for controlling gaseous pollutants since it has a relatively simple structure compared to other possible control devices, and therefore, can be coupled without much difficulty with various moving and stationary sources. The mathematical model for a fixed bed adsorption process generally takes into account the dynamic changes of adsorbate concentrations in both gaseous and solid phases at various positions of the bed. Modeling of the concentration dynamics can usually be accomplished either by taking a mass balance (for an isothermal process) or by taking mass and energy balances (for a nonisothermal process) over a control volume of the bed.

In the modeling of adsorption processes in fixed beds, external mass transfer, intraparticle diffusion, or surface adsorption, or a combination of these processes is usually considered to be rate controlling. The external mass tranfer control model is applicable for cases where the adsorbent particles are relatively small. The intraparticle diffusion control model is often used for relatively large adsorbent particles. The significance of this adsorbate transport step has been verified by Masamune and Smith[1], and Rimple, et al.[2]. The surface adsorption control model is valid only when relatively small resistances are imposed by the external mass transfer and intraparticle diffusion steps. A combined rate control model of external mass transfer and intraparticle diffusion has also been used[1].

Since the rate of adsorption depends on the degree of saturation of adsorbate on adsorbent, knowledge of the equilibrium phenomenon is

required in modeling the adsorber performance. Models for various types of equilibrium states have been extensively delineated [3,4]. While a linear equilibrium equation is often used because of its simplicity, many of the available equilibrium models give rise to nonlinear equations; among them are the Langmuir's monolayer theory, Polanyi's potential theory, capillary condensation theory, Freunlich's model, and BET model.

The flow pattern of the gas in a fixed bed adsorber also affects significantly its performance. Although the flow pattern in the fixed bed adsorber is very difficult to be accurately described mathematically, it can be approximated by various models; for example, the back-mix (completely mix) flow model, the plug flow model, and nonideal flow models such as the dispersion model, the compartment model, and the combined or mixed model[5,6]. Among these, the plug flow and axial dispersion models are the two most frequently employed. The plug flow model is valid if the adsorber bed is relatively deep and the movement of the adsorbate is predominated by the convective motion. The model has been extensively used in modeling both the isothermal[1,7-10] and nonisothermal[11-13] adsorption processes in fixed beds.

The actual flow pattern of a gas through a fixed adsorption bed can deviate appreciably from that represented by the plug flow. Axial dispersion of the adsorbate can be caused by the turbulence, influence of the velocity profile, molecular diffusion, and convective mixing due to temperature differences. Therefore, the dispersion model is more realistic than the plug flow model to simulate the flow through a fixed bed, especially for a shallow bed. However, the application of this model has been limited thus far to the isothermal case for adsorption

processes[14-18] although it has been extensively employed to simulate nonisothermal or adiabatic processes for packed bed catalytic reactions[19-21].

In this study, the adiabatic adsorption process taking place in a fixed bed of adsorbent is mathematically modeled and numerically simulated. The flow of the gas phase in the bed is modeled by the axial dispersion model. The mass and heat transfers between the gas and solid phases are assumed to be external transfer rate controlling while the equilibrium istherm between the two phases is assumed to be that of the Langmuir type. Computer simulation is used to examine the effects of various design parameters such as the Peclet number, external mass and heat transfer coefficients, and the adsorbent capacity on the dynamic changes in the adsorbate concentration and temperature in both gaseous and solid phases of the bed.

3.1. MODEL EQUATIONS AND NUMERICAL SOLUTIONS

The assumptions made in deriving the model equations for the packed adsorber under consideration are that

(a) An adsorption process taking place in a fixed bed is adiabatic,

(b) Parameters such as heat and mass transfer coefficients, porosity of bed, adsorbent density, specific surface area, specific heats of gas and adsorbent, heat conductivity of adsorbent do not change with operating conditions, and

(c) No dispersion of the gaseous components occurs in the entrance and exit sections adjacent to the bed.

Mass and heat balances over a control volume of the bed lead to the following partial differential equations.

$$H_g \frac{\partial c}{\partial t} = \Phi \rho_g E_1 \frac{\partial^2 c}{\partial z^2} - G \frac{\partial c}{\partial z} - R_a \tag{1}$$

$$H_s \frac{\partial q}{\partial t} = R_a \tag{2}$$

$$H_g c_g \frac{\partial T_g}{\partial t} = \Phi E_2 \frac{\partial^2 T_g}{\partial z^2} - G c_g \frac{\partial T_g}{\partial z} - ha(T_g - T_a) \tag{3}$$

$$H_s c_s \frac{\partial T_a}{\partial t} = (1-\Phi) E_3 \frac{\partial^2 T_g}{\partial z^2} + ha(T_g - T_a) + (\Delta H_a) R_a \tag{4}$$

The initial and boundary conditions are:

when $t = 0$

$$c = 0 \tag{5}$$

$$q = 0 \tag{6}$$

$$T_g = T_0 \tag{7}$$

$$T_a = T_0 \tag{8}$$

at $z = 0$

$$G\,(c)\Big|_{z=0^+} = C c_f + \Phi \rho_g E_1 \left(\frac{\partial c}{\partial z}\right)\Big|_{z=0^+} \tag{9}$$

$$G\, c_g (T_g)\Big|_{z=0^+} = G c_g T_0 + \Phi E_2 \left(\frac{\partial T_g}{\partial z}\right)\Big|_{z=0^+} \tag{10}$$

$$\frac{\partial T_a}{\partial z} = 0 \tag{11}$$

at $z = L$

$$\frac{\partial c}{\partial z} = 0 \tag{12}$$

$$\frac{\partial T_g}{\partial z} = 0 \tag{13}$$

$$\frac{\partial T_a}{\partial z} = 0 \tag{14}$$

The adsorption rate, R_a, for the external mass transfer control mechanism can be written as

$$R_a = k_e\, a\, \rho_g (c - c^*) \tag{15}$$

where c* is the gas phase equilibrium concentration which can be expressed by a Langmuir type isotherm

$$q = \frac{q_m\, bc^*}{1 + bc^*} \tag{16}$$

where

$$b = \frac{A_1 \exp(\frac{A_2}{T_a})}{T_a^{\frac{1}{2}}} \tag{17}$$

Let

$$\begin{aligned} X &= \frac{c}{c_f} \\ Y &= \frac{q}{q_m} \\ U &= \frac{T_g}{T_0} \\ V &= \frac{T_a}{T_0} \end{aligned} \tag{18}$$

$$\lambda = \frac{z}{L}$$

$$\tau = \frac{t\,G}{L\,H_g}$$

$$Pe_m = \frac{GL}{\Phi \rho_g E_1}$$

$$Pe_h = \frac{GL}{\Phi \rho_g \left(\frac{E_2}{\rho_g c_g}\right)} = \frac{GL}{\Phi \rho_g E_2'} \quad \left(E_2' = \frac{E_2}{\rho_g c_g}\right)$$

$$K_e = \frac{k_e a \rho_g L}{G}$$

$$H = \frac{haL}{G c_g}$$

$$K = \frac{(1-\Phi) E_3 H_g}{G\,L\,H_s}$$

$$\alpha = \frac{H_g c_f}{H_s q_m}$$

$$\beta = \frac{H_g c_g}{H_s c_s}$$

$$\gamma = \frac{(\Delta H_a) H_g c_f}{c_s H_s T_0}$$

Then equations (1) through (16) can be transformed into

$$\frac{\partial X}{\partial \tau} = \frac{1}{Pe_m} \frac{\partial^2 X}{\partial \lambda^2} - \frac{\partial X}{\partial \lambda} - K_e (X - X^*) \tag{19}$$

$$\frac{\partial Y}{\partial \tau} = \alpha K_e (X - X^*) \tag{20}$$

$$\frac{\partial U}{\partial \tau} = \frac{1}{Pe_h} \frac{\partial^2 U}{\partial \lambda^2} - \frac{\partial U}{\partial \lambda} - H(U - V) \tag{21}$$

$$\frac{\partial V}{\partial \tau} = K \frac{\partial^2 V}{\partial \lambda^2} + \beta H(U - V) + \gamma K_e (X - X^*) \tag{22}$$

$$Y = \frac{BX^*}{1 + BX^*} \tag{23}$$

The corresponding initial and boundary conditions are:

when $\tau = 0$

$$X = 0 \tag{24}$$

$$Y = 0 \tag{25}$$

$$U = 1 \tag{26}$$

$$V = 1 \tag{27}$$

at $\lambda = 0$

$$(X)\Big|_{\lambda=0^+} = 1 + \frac{1}{Pe_m} \left(\frac{\partial X}{\partial \lambda}\right)\Big|_{\lambda=0^+} \tag{28}$$

$$(U)\Big|_{\lambda=0^+} = 1 + \frac{1}{Pe_h} \left(\frac{\partial U}{\partial \lambda}\right)\Big|_{\lambda=0^+} \tag{29}$$

$$\frac{\partial V}{\partial \lambda} = 0 \tag{30}$$

at $\lambda = 1$

$$\frac{\partial X}{\partial \lambda} = 0 \tag{31}$$

$$\frac{\partial U}{\partial \lambda} = 0 \tag{32}$$

$$\frac{\partial V}{\partial \lambda} = 0 \tag{33}$$

where

$$B = \frac{A_1' \exp(\frac{A_2'}{V})}{(V)^{\frac{1}{2}}} \tag{34}$$

If the mass dispersion coefficient, E_1, is assumed to be equal to the thermal dispersion coefficient, E_2' (or $E_2/\rho_g c_g$), then

$$Pe_m = Pe_h = Pe \tag{35}$$

It would be very difficult, if not impossible, to obtain analytical solutions for the simultaneous partial differential equations, equations (19) through (23), subject to the initial and boundary conditions, equations (24) to (33). Computer-aided numerical methods can be employed for solution. These methods include the finite difference method, method of characteristics, and collocation method. Among these, the implicit finite difference method, specifically the Crank-Nicolson method, is employed in this study. The method involves less stringent stability and convergence restrictions than the explicit finite difference method and requires less computing time than the method of characteristics. In addition, this method is known to be particularly powerful for the parabolic partial differential equations encountered in this study

In employing the Crank-Nicolson method, each partial differential equation is rewritten as a set of simultaneous algebraic equations. Since a detailed description of the method is available elsewhere[22,23], the derivation of the simultaneous algebraic equations and the solution thereof by using the Thomas algorithm are not given here.

3.2. RESULTS AND DISCUSSIONS

The Langmuir type isotherm given in equation (23) is plotted in Figure 1 for $A_1' = 1.35 \times 10^{-6}$ and $A_2' = 15.04$. This isotherm is employed throughout this study. Figure 2 shows the adsorbate concentration distributions in a packed bed adsorber for different values of operating time. The adsorbate concentrations in the gaseous and solid phasas of the bed are initially zero. When adsorbate laden gas is introduced, the adsorbate penetrates into the void in the bed by convection and diffusion, and simultaneously the adsorption process takes place between the adsorbate in the void and the surface of the adsorbent. This results in the gas phase adsorbate concentration profile decreasing in the axial direction of flow. As time increases, the adsorbent surface is gradually saturated and the adsorbate concentration in the gaseous phase becomes higher. As τ approaches infinity, the adsorbent is completely saturated and the exit concentration becomes the same as the inlet concentration. At the same time, the adsorbate concentration on the adsorbent assumes the equilibrium value with respect to the inlet concentration at the inlet temperature. The effect of dispersion results in the adsorbate concentration drop at the entrance of the bed as shown in Figure 2. The magnitude of the concentration drop depends on the intensity of dispersion expressed in terms of the Peclet number and the magnitude of the concentration gradient.

Figure 3 shows the temperature distributions of the gas and solid phases. The temperatures are assumed to be initially identical with the room temperature (or the inlet gas temperature). Heat released from the adsorption process raises the adsorbent temperature as well as the gas phase temperature. The maximum gas and solid phase temperatures occur initially at the entrance

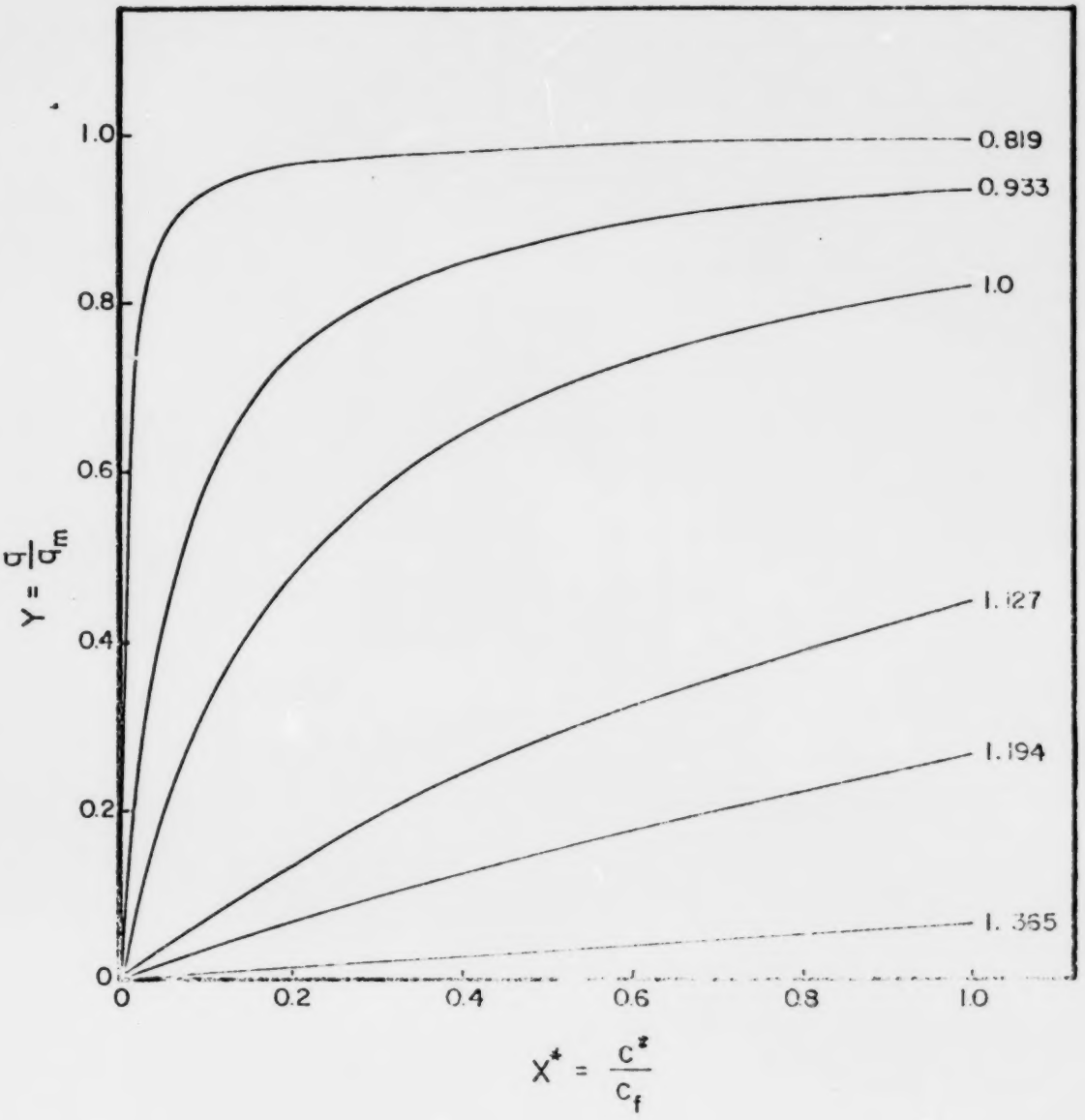

Fig. 1. Adsorption isotherm plotted according to a Langmuir type isotherm, equation (23) (parameter, V).

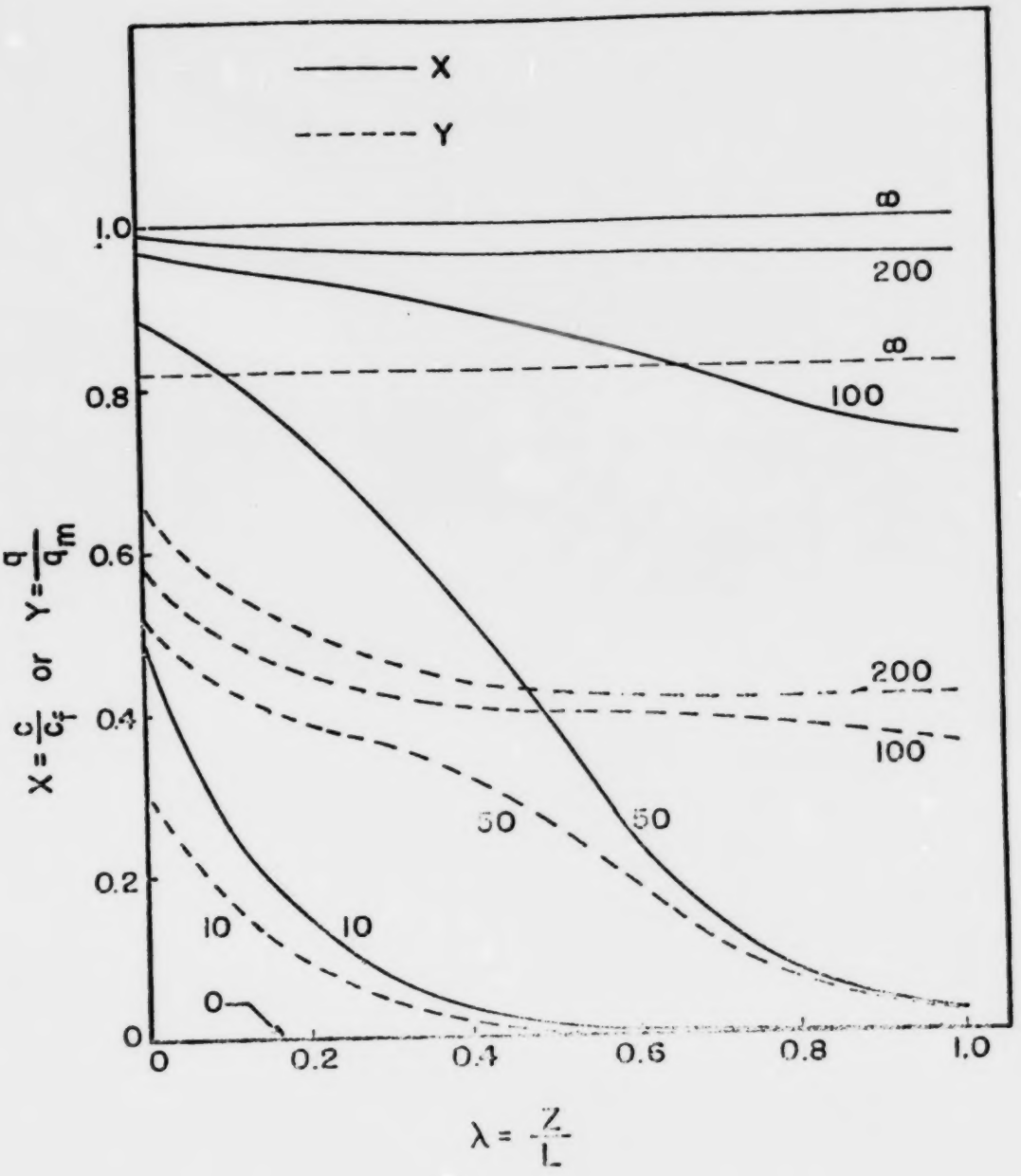

Fig. 2. Adsorbate concentration distribution in a packed bed adsorber (P_s=5, K_s=20, H=100, α=0.005, β=0.001, γ=0.002, parameter, τ).

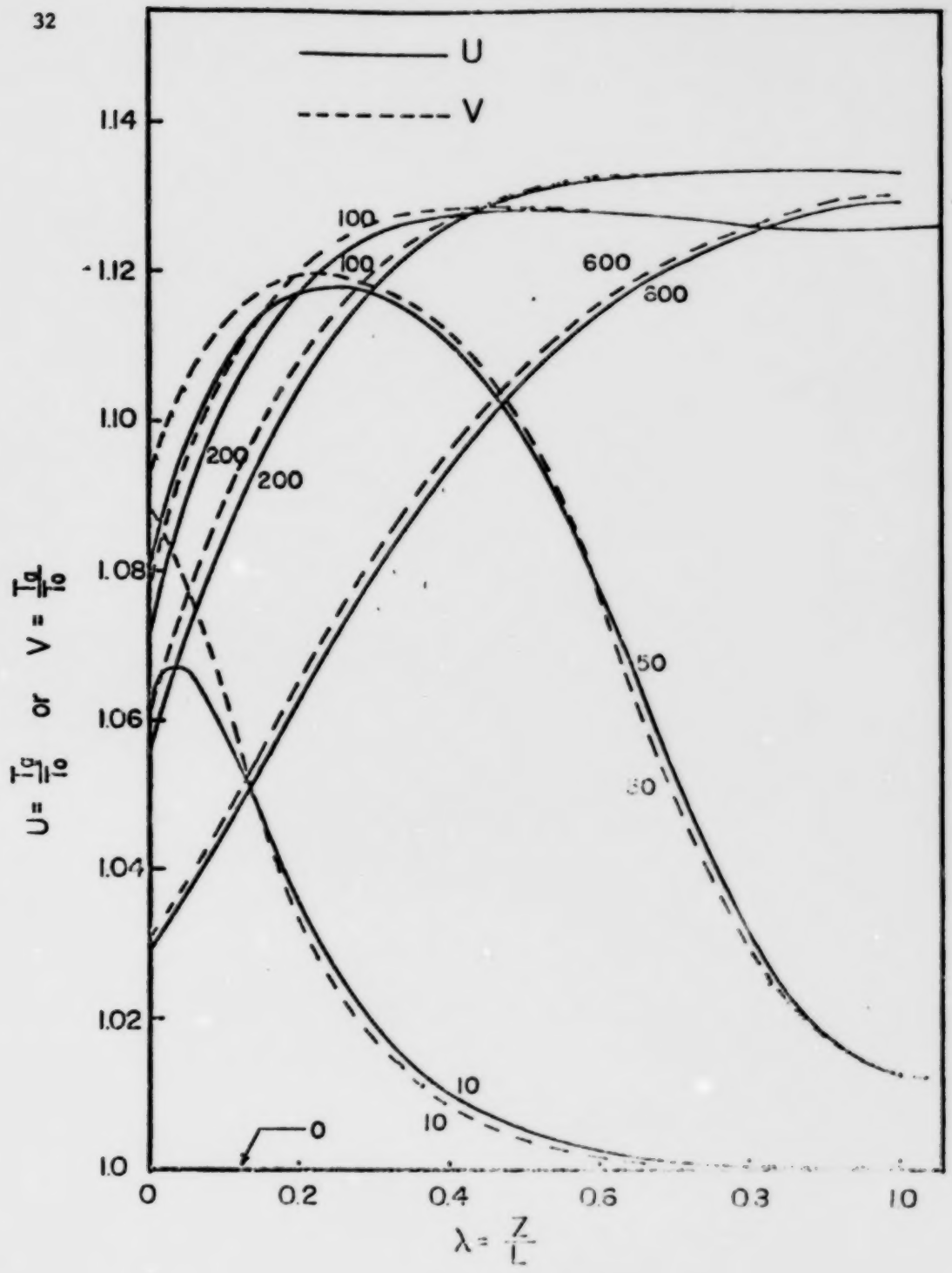

Fig. 3. Temperature distribution in a packed bed adsorber ($P_3 = 5$, $K_e = 20$, $H = 100$, $\alpha = 0.005$, $\beta = 0.001$, $\gamma = 0.002$, parameter, ϵ).

of the bed and gradually move in the direction of gas flow as the zone of maximum adsorption rate moves in the same direction. The maximum gas temperature always appears at a distance farther down the bed than the maximum adsorbent temperature due to the convection of heat in the gas phase in the direction of flow. The effect of dispersion on the jump in the gas temperature at the entrance can also be observed in Figure 3. The temperature gradient in the gas phase generated by the heat of adsorption causes heat to be dispersed in the directions along and opposite to the gas flow. Since no heat is transported out of the bed into the entrance section, heat dispersed in the direction opposite to the gas flow is reflected into the bed at the entrance. This renders the gas phase temperature at the entrance of the bed to be higher than the incoming gas temperature. This phenomenon is especially pronounced at the onset of the operation. When time τ approaches infinity, the bed temperature becomes the same as the incoming gas temperature because the rate of heat generation decreases with an increase in the degree of saturation of the adsorbate on the adsorbent, and the heat generated is rapidly removed by the gas flowing through the bed.

The effect of dispersion as characterized by the Peclet number on the concentration in the gas phase of the bed at $\tau = 100$ for different values of the heat of adsorption is shown in Figure 4, and that in the solid phase in Figure 5. As expected, these figures show that the adsorbate concentration are uniform throughout the bed when Pe = 0 (complete mixing). For large values of Pe, e.g. Pe = 500, the flow behavior is essentially that of the plug flow. For intermediate values of Pe, namely for a finite degree of dispersion, the adsorbate concentration profiles fall between the profiles for complete mixing and that for plug flow. The effect of heat of adsorption is also clearly shown in the figures. Figure 4 shows that, for the same value of the Peclet number, the average adsorbate concentration in the gas phase is

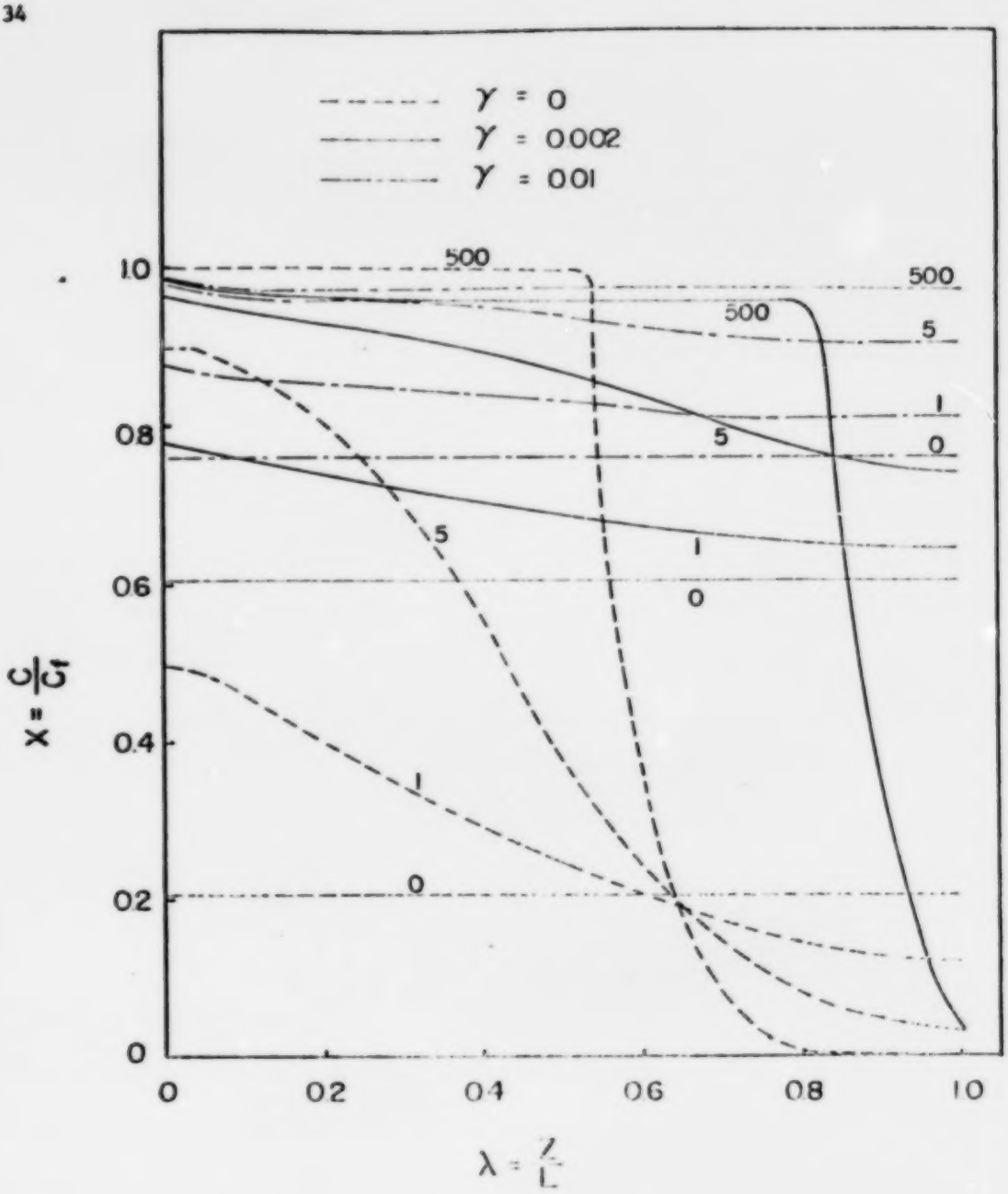

Fig. 4. Effect of Peclet number on the gas phase adsorbate concentration distribution in a packed bed adsorber at $\tau = 100$ ($K_3 = 20$, $H = 100$, $\alpha = 0.005$, $\beta = 0.001$; Parameter, P_3).

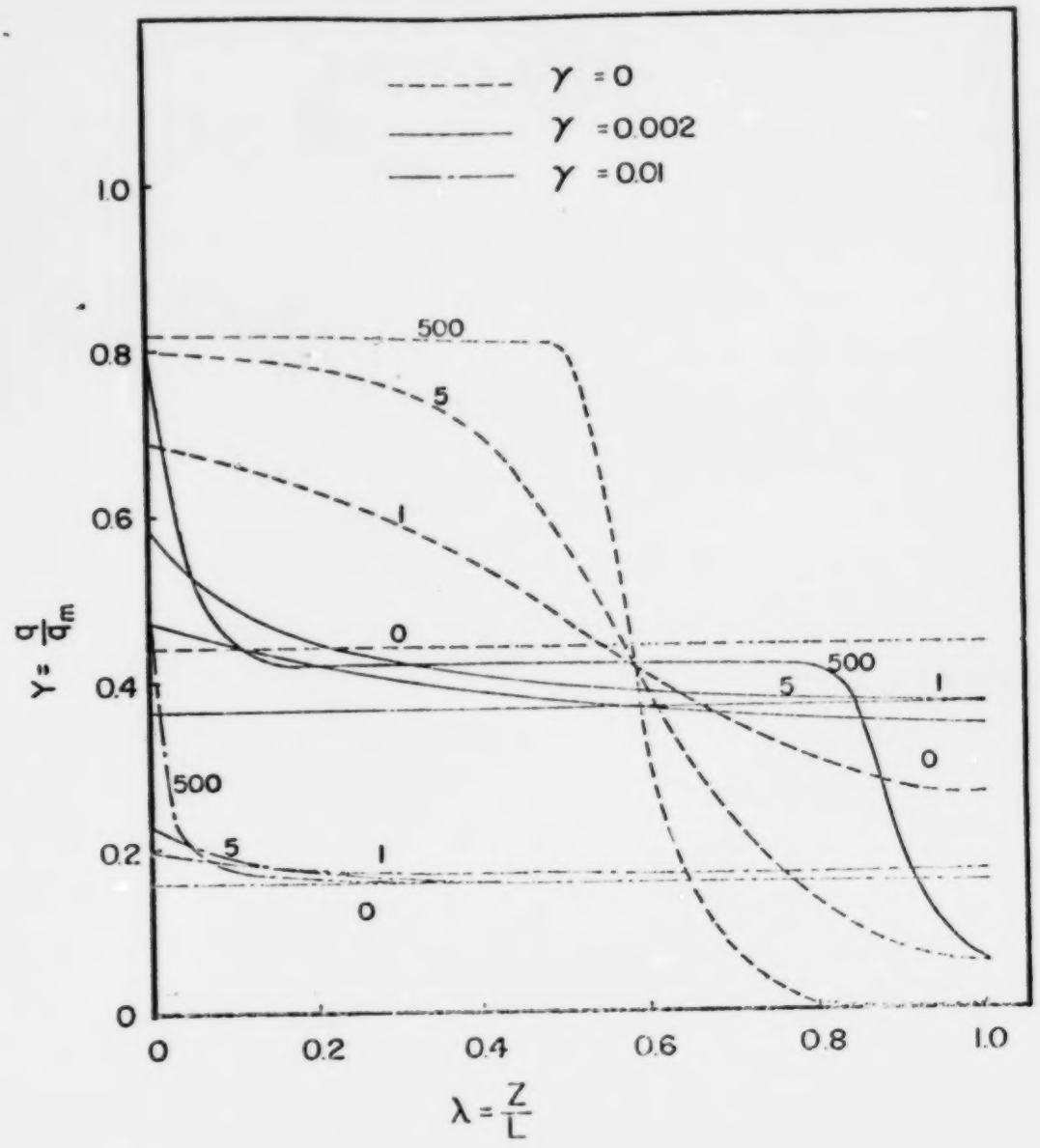

Fig. 5. Effect of Peclet number on the solid phase adsorbate concentration distribution in a packed bed adsorber at $\tau = 100$ (K_e=20, H=100, α =0.005, β=0.001; parameter, γ).

lower for the isothermal case ($\gamma = 0$) than for the non-isothermal case ($\gamma > 0$). Conversely, Figure 5 shows that the average adsorbate concentration in the solid phase is higher for the isothermal case than for the non-isothermal case. In other words, the adsorption process proceeds faster in an isothermal bed than in a non-isothermal bed. This is because the heat generated from the adsorption process in a non-isothermal bed raises the solid phase temperature, thus resulting in a smaller driving force for adsorbate transfer.

The effect of dispersion on the temperature distributons in the gas and solid phases in the bed is shown in Figure 6. For Pe = 0 (complete mixing), the temperature profiles are flat across the bed as expected. The solid phase temperature is higher than the gas phase temperature because heat is generated in the solid phase, raising the solid phase temperature first, and then is transported to the gas phase. When the Peclet number increases, the temperatures in both phases increase sharply near the entrance and then level off. For very large values of the Peclet number, e.g. Pe = 500, the temperatures drop sharply near the exit. This is reasonable since little adsorption has occurred near the exit as reflected by Figures 4 and 5.

Figure 7 shows the effect of dispersion on the breakthrough of the incoming gas. For small values of the Peclet number, the dispersion of the gas is so intensive that the adsorbate is almost uniformly distributed in the bed. The adsorbate concentration in the gas phase near the exit is almost the same as that near the entrance. Therefore, the adsorbate breaks through the bed fairly rapidly. For large values of the Peclet number, however, the gas is not well dispersed. The bed is saturated with the adsorbate progressively from the entrance toward the exit. The adsorbate does not move downstream either by convection or by diffusion unless it finishes saturating the portion of the bed it has contacted. Thus a moving front is

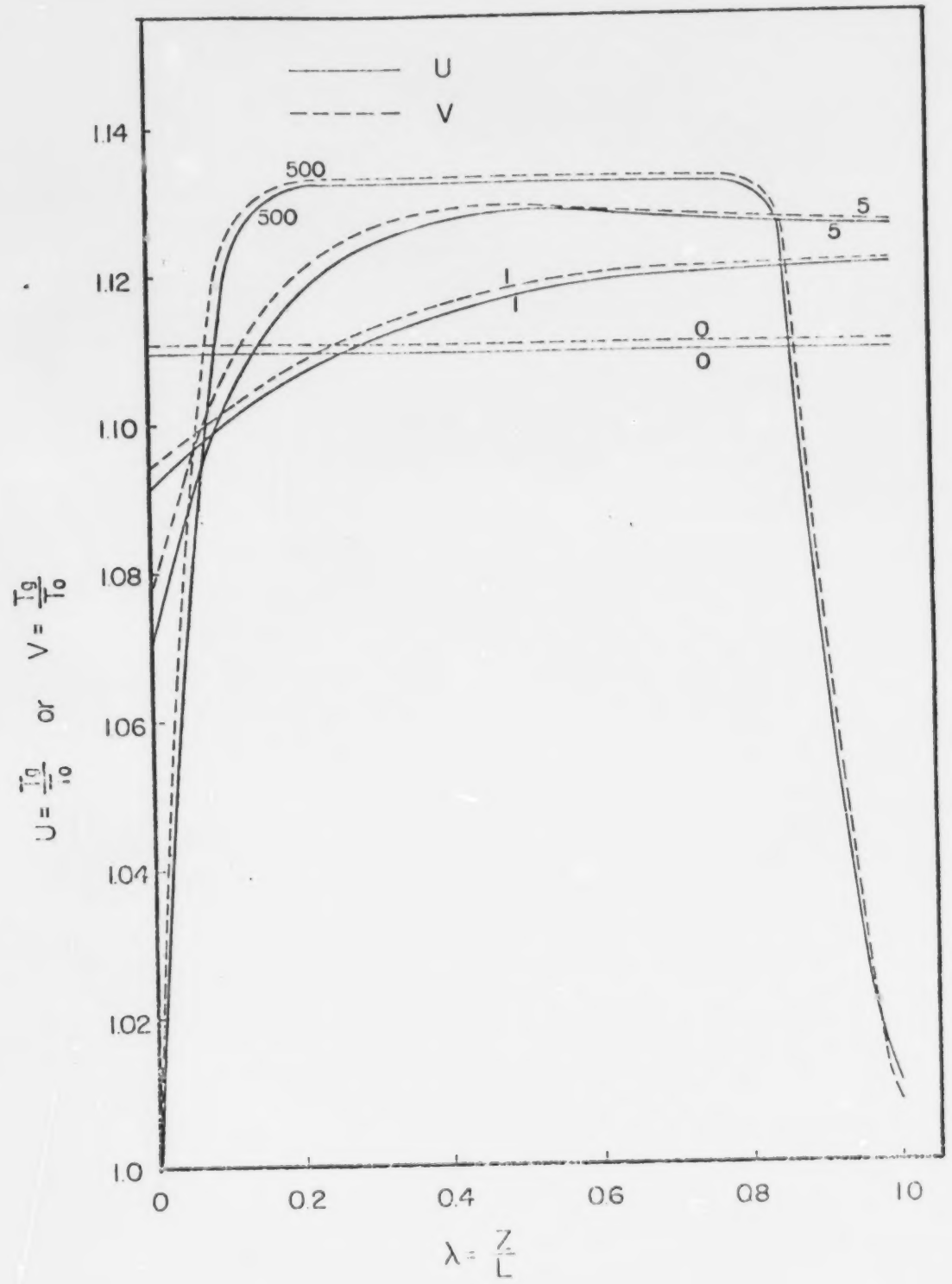

Fig. 6. Effect of Peclet number on the temperature distribution in a packed bed adsorber at $\tau = 100$ ($K_g = 20$, $H = 100$, $\alpha = 0.005$, $\beta = 0.001$, $\gamma = 0.002$; parameter, P_e).

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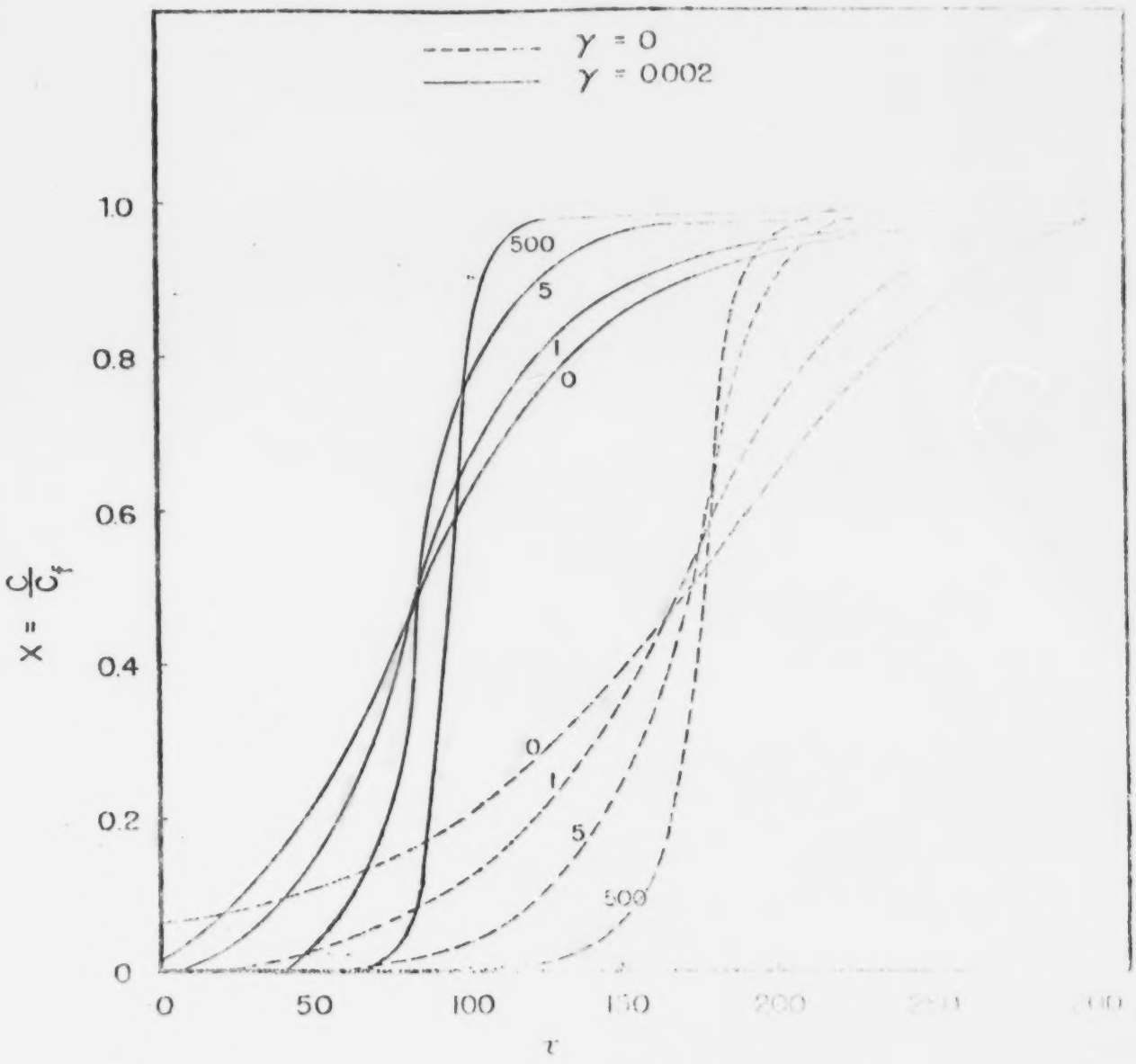

Fig. 7. Effect of Peclet number on the [illegible] concentration change in a packed bed adsorber, (K_a = 20, H = 100, α = 0.005, β = 0.001; parameter, γ).

formed which separates the bed into two distinct portions: one with complete contamination and the other no contamination. In this manner, the breakthrough occurs relatively late and sharply. It is worth noting that, for the same value of the Peclet number, the breakthrough occurs earlier for the non-isothermal process than for the isothermal process.

Figure 8 shows the effect of dimensionless external mass transfer coefficient, K_e, on the adsorbate concentration distribution. For $K_e = 0$, no adsorption takes place in the bed, and therefore, the void space of the bed is completely filled with the incoming gas and the adsorbent remains uncontaminated. For K_e values other than zero, the concentrations of both the gas and solid phases in the bed are higher for large values of K_e than for small values of K_e since the bed is saturated more rapidly for large value of K_e.

Figure 9 shows the effect of α, the inverse of the adsorption capacity of the bed, on the transient adsorbate concentration at the exit for three different values of the heat of adsorption. For $\alpha = 0$, or $1/\alpha \to \infty$, the bed has infinite adsorption capacity and is never saturated. For large values of α, or small values of $1/\alpha$, the adsorption capacity is small; therefore, the bed is rapidly saturated. The effect of α on the solid phase temperature distribution in the bed is shown in Figure 10. For small values of α, more adsorbate can be adsorbed and more heat is generated in the bed. This may result in very high temperatures in the bed. In particular, for $\alpha = 0$, the bed temperature may rise continuously with time until heat generation is equal to heat removal by gas flow. In this case, the adsorber temperature may rise to a very high level, and consequently the stability problem becomes serious.

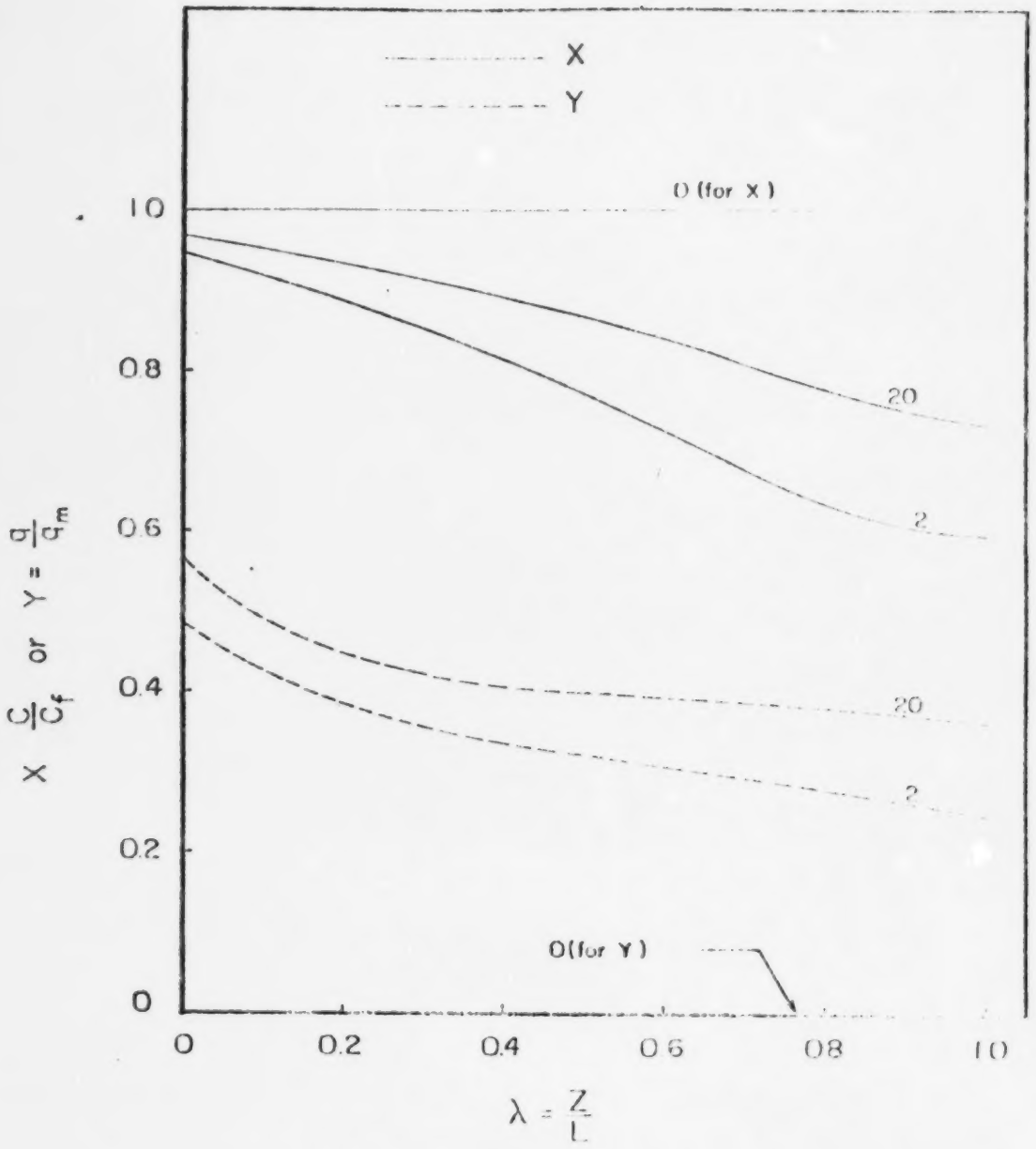

Fig. 8. Effect of K_3 on the adsorbate concentration distribution in a packed bed adsorber at $\tau = 100$ ($P_1 = 5$, $H = 100$, $\alpha = 0.005$, $\beta = 0.001$, $\gamma = 0.002$; parameter, K_3).

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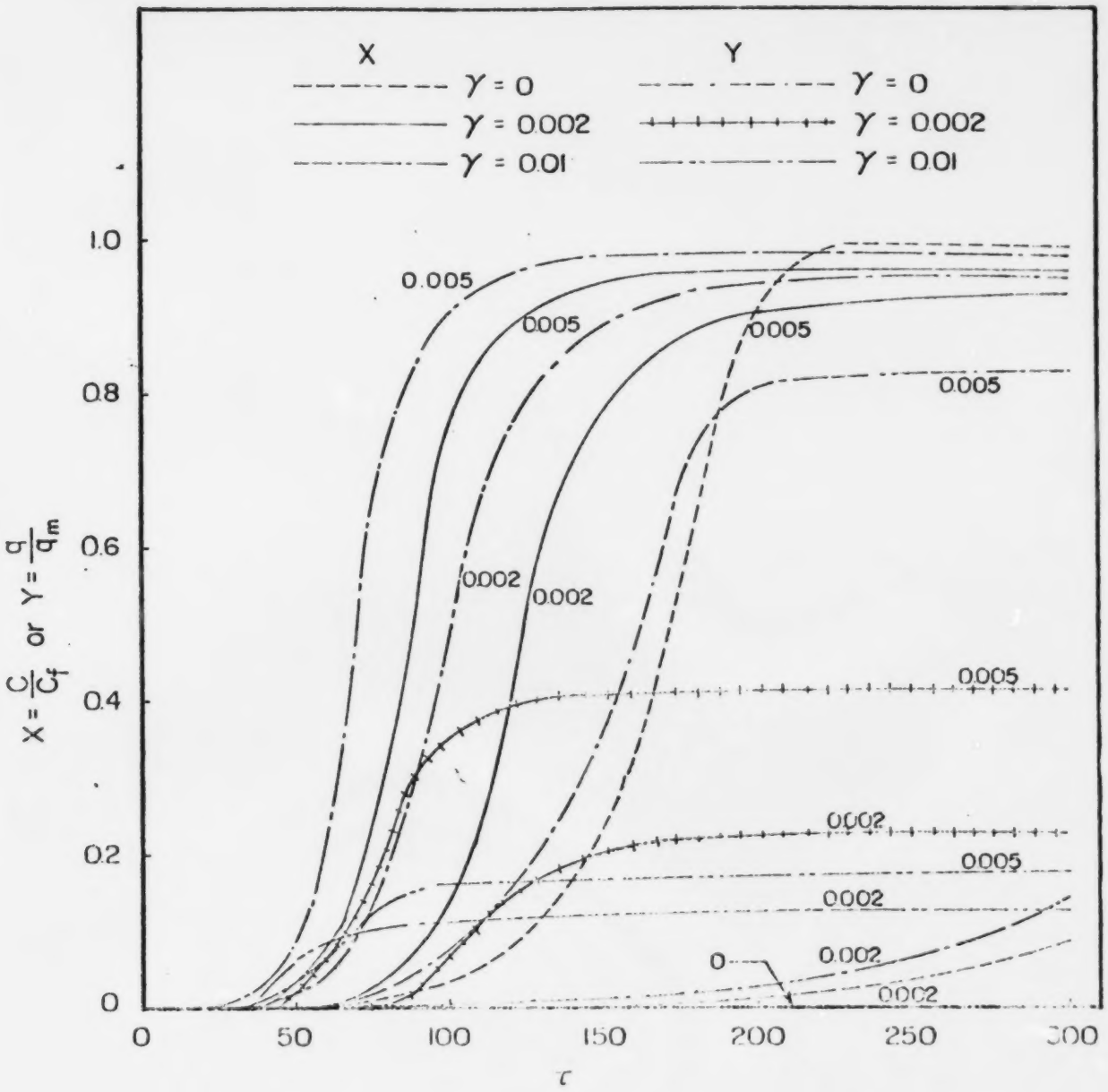

Fig. 9. Effect of α on the exit adsorbate concentration change in a packed bed adsorber ($P_e = 5$, $K_e = 20$, $H = 100$, $\beta = 0.001$; parameter, α).

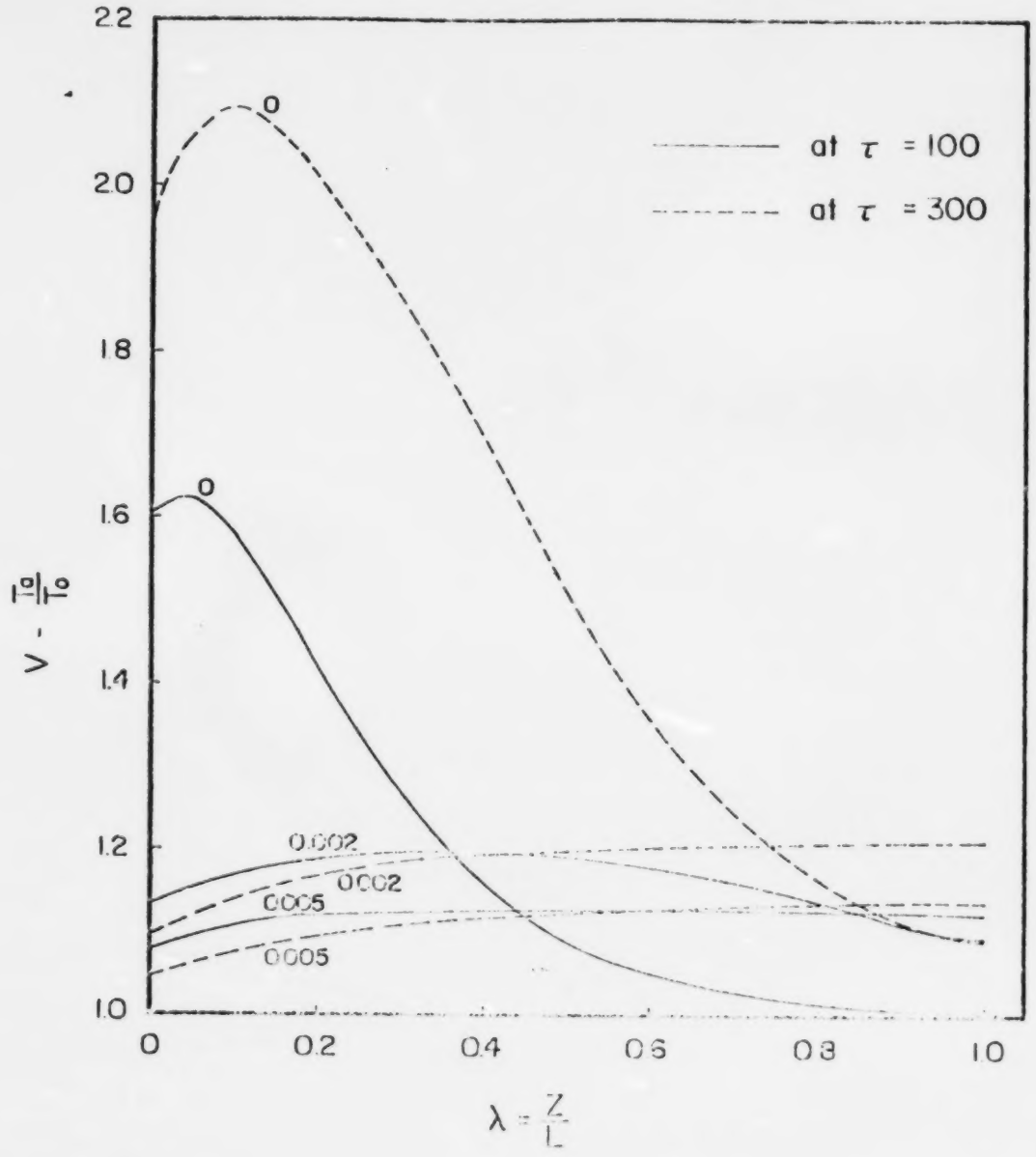

Fig. 10. Effect of α on the solid phase temperature distribution in a packed bed adsorber (P_e=6, K_e=20, H=100, β=0.001, γ=0.002; parameter, α)

A further insight into the operation of an adsorber unit can be gained through evaluation of accumlated adsorption efficiency. A macroscopic adsorbate balance over the total volume of the bed gives

$$C_f\, Gt = \int_0^t C_e\, G\, dt + \int_0^L C\, H_g\, dz + \int_0^L q\, H_s\, dz \qquad (36)$$

By introducing dimensionless quantities in equation (18), equation (36) can be rewritten as

$$\tau = \int_0^\tau X_e\, d\tau + \int_0^1 X\, d\lambda + \frac{1}{\alpha} \int_0^1 Y\, d\lambda \qquad \text{if } \alpha \neq 0$$

or (37)

$$\tau = \int_0^\tau X_e\, d\tau + \int_0^1 X\, d\lambda \qquad \text{if } \alpha = 0$$

Thus the accumlated adsorption efficiency can be defined as

$$\eta_a = 1 - \frac{1}{\tau} \int_0^\tau X_e\, d\tau \qquad (38)$$

or (39)

$$\eta_a = \frac{1}{\tau} \left\{ \int_0^1 X\, d\lambda + \frac{1}{\alpha} \int_0^1 Y\, d\lambda \right\} \qquad \text{if } \alpha \neq 0$$

$$= \frac{1}{\tau} \int_0^1 X\, d\lambda \qquad \text{if } \alpha = 0$$

Note that the adsorption efficiency changes with time and can be obtained by integrating either equation (38) or (39) numerically. Table 1 shows the accumulated removal efficiencies for the nominal case at different times. The computational results by using both equations, viz. equations (38) and (39)

Table 1. Accumulated adsorption efficiency for the nominal standard case.

time, τ	adsorption efficiency, η_a	
	equation (38)	equation (39)
50	0.9930	0.9874
100	0.8436	0.8422
150	0.6001	0.5998
200	0.4607	0.4606
250	0.3762	0.3760
300	0.3197	0.3196

are almost identical, indicating that the numerical scheme employed in this study is reliable.

Figure 11 shows the effect of axial dispersion characterized by the Peclet number on the accumulated adsorption efficiency. The adsorption efficiency is generally increased when dispersion is less significant and vice versa. In all cases, the accumulated adsorption efficiency decreases as time increases because the bed becomes saturated gradually. The effect of heat of adsorption, γ, is also shown in the figure. It is readily seen that the accumulated adsorption efficiencies are lower for the nonisothermal cases ($\gamma > 0$) than for the isothermal case ($\gamma = 0$).

The effect of the inverse adsorption capacity α on the accumulated adsorption efficiency at different values of γ is shown in Figure 12. When α is small the adsorption capacity of the bed is large, resulting in slow saturation of the bed and consequently, in a high accumulated adsorption efficiency.

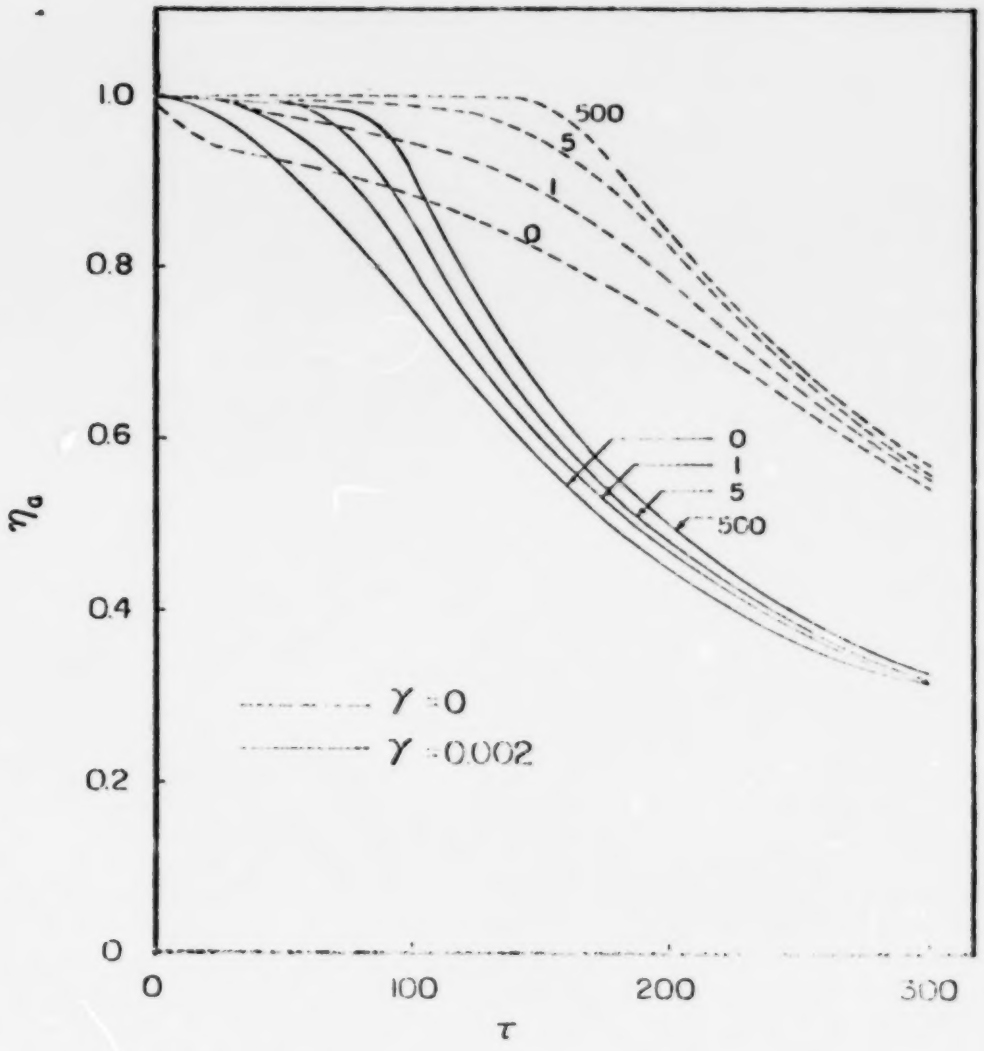

Fig. 11. Effect of Peclet number on the accumulated adsorbate removal efficiency (K_a=20, H=100, α=0.005, β=0.001; parameter, P_e).

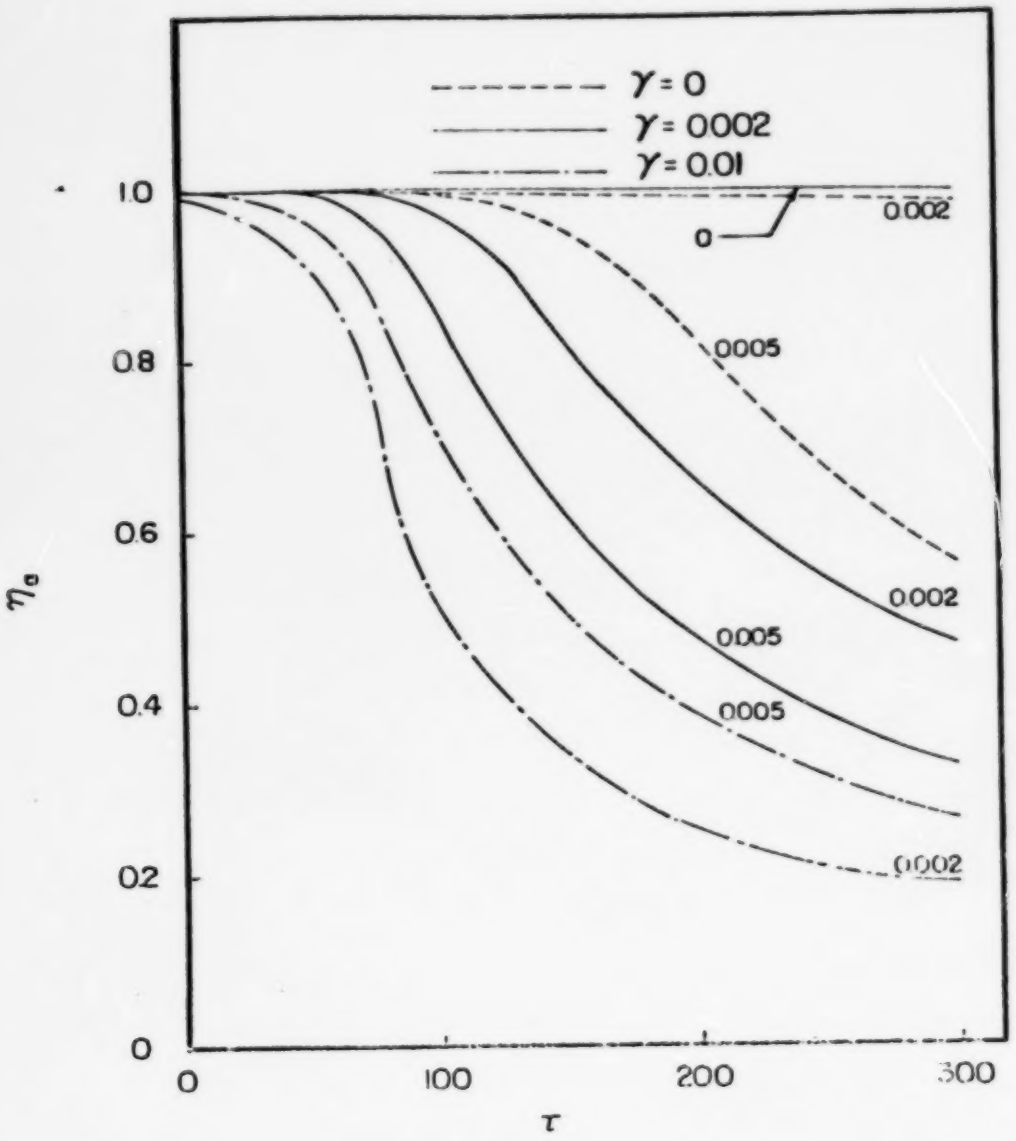

Fig. 12. Effect of α on the accumulated adsorbate removal efficiency (P_e = 5, K_a = 20, H = 100, β = 0.001; parameter, α).

NOMENCLATURE

a = available external surface area per unit volume of bed, cm^2/cm^3

A_1 = constant $(^oK)^{1/2}$

A_1' = constant, $\frac{c_f A_1}{(T_0)^{\frac{1}{2}}}$

A_2 = constant, ^oK

A_2' = constant, $\frac{A_2}{T_0}$

b = adsorption coefficient expressed equation (17)

B = constant expressed in equation (34)

c = adsorbate concentration in gas phase, g of adsorbate/g of adsorbate free gas

c^* = equilibrium concentration, g of adsorbate/g of adsorbate free gas

c_f = feed concentration, g of adsorbate/g of adsorbate free gas

c_g = specific heat of gas, cal/^oK-g

c_s = specific heat of solid adsorbent, cal/^oK-g

E_1 = axial mass dispersion coefficient in the gas phase, cm^2/sec

E_2 = axial dispersive conductivity of the gas phase, cal/sec. ^oK-cm

E_2' = axial thermal dispersion coefficient in the gas phase, cm^2/sec

E_3 = thermal conductivity of solid, cal/sec-^oK-cm

G = superficial mass flow rate of fluid per unit cross-sectional area, g of gas/sec-cm^2

h = heat transfer coefficient between gas and adsorbent, cal/^oK-cm^2-sec

H = dimensionless heat transfer coefficient, $\frac{hal.}{Gc_g}$

H_g = gas phase hold-up, i.e., mass of gas per unit volume of bed, g of gas/cm^3 of bed

H_s = solid phase hold-up, i.e., mass of adsorbent per unit volume of bed, g of adsorbent/cm^3 of bed

ΔH_a = average heat of adsorption, cal/g

k_e = external mass transfer coefficient based on external surface of particle and concentration driving force, cm/sec

K = dimensionless adsorbent heat conductivity, $\frac{(1-\Phi)E_3 H_g}{G\ L\ H_s}$

K_e = dimensionless mass transfer coefficient, $\frac{k_e a \rho_g L}{G}$

L = depth of adsorption bed, cm

Pe = Peclet number

Pe_h = Peclet number for heat transfer, $\frac{GL}{\Phi \rho_g E_2}$

Pe_m = Peclet number for mass transfer, $\frac{GL}{\Phi \rho_g E_1}$

q = amount of adsorbate adsorbed per unit mass of adsorbent, g of adsorbate/g of adsorbent

q_m = maximum amount of adsorbate which can be adsorbed per unit mass of adsorbent, g of adsorbate/g of adsorbent

R_a = overall rate of adsorption per unit volume of bed, g/sec-cm^3

t = time, sec

T_a = adsorbent temperature, ^oK

T_g = gas temperature, ^oK

T_0 = temperature at the inlet of the bed, ^oK

U = dimensionless gas temperature, $\frac{T_g}{T_0}$

V = dimensionless adsorbent temperature, $\frac{T_a}{T_0}$

X = dimensionless adsorbate concentration in gas phase, $\frac{c}{c_f}$

X^* = dimensionless adsorbate equilibrium concentration in gas pahse, $\frac{c^*}{c_f}$

Y = dimensionless adsorbate concentration in solid phase, $\frac{q}{q_m}$

z = axial distance from entrance of bed, cm

GREEK LETERS

α = inverse of the adsorption capacity of the bed, $\frac{H_g c_f}{H_s q_m}$

β = ratio of heat capacity of gas phase to that of solid phase in the bed, $\frac{H_g c_g}{H_s c_s}$

γ = dimensionless heat of adsorption, $\frac{(\Delta H_a) H_g c_f}{c_s H_s T_0}$

η_a = accumulated adsorption efficiency

λ = dimensionless axial distance, $\frac{z}{L}$

ρ_g = density of gas, g/cm^3

τ = dimensionless time, $\frac{tG}{L H_g}$

Φ = void fraction of the bed

REFERENCES

1. Masamune, S. and J. M. Smith, AIChE Journal, 10, 246 (1964).

2. Rimpel, A. E., Jr., D. T. Camp, J. A. Kostecki, and L. N. Canjar, AIChE Journal, 14, 19 (1968).

3. Brunauer, S., "The Adsorption of Gases and Vapors, Volume I, Physical Adsorption," Princeton University Press, Princeton, N. J. (1943).

4. Young, D. M. and A. D. Crowell, "Physical Adsorption of Gases," Butterworth, London (1962).

5. Deans, H. A. and L. Lapidus, AIChE Journal, 6, 656 (1960).

6. Wen, C. Y. and L. T. Fan, "Models for Flow Systems," Monograph to be published, Gordon and Breach, New York (1974).

7. Lee, R. G. and T. W. Weber, Can. J. Chem. Eng., 47, 54 (1969).

8. Gariepy, R. L. and I. Zwiebel, "Adsorption of Binary Mixtures in Fixed Beds," a paper presented at the 68th National Meeting of the AIChE, Houston, Texas, Feb. 28 - March 4 (1971).

9. Thomas, W. J. and J. L. Lombardi, Trans. Instn. Chem. Engrs., 49, 240 (1971).

10. Carter, J. W. and H. Husain, Trans. Instn. Chem. Engrs., 50, 69 (1972).

11. Carter, J. W., Trans. Instn. Chem. Engrs., 44, T253 (1966).

12. Meyer, O. A. and T. W. Weber, AIChE Journal, 13, 457 (1967).

13. Lee, R. G. and T. W. Weber, Can. J. Chem. Eng., 47, 60 (1969).

14. Schneider, P. and J. M. Smith, AIChE Journal, 14, 762 (1968).

15. Chu, C. and L. C. Tsang, Ind. Eng. Chem. Process Des. Develop., 10, 47 (1971).

16. Cooney, D. O. and F. P. Strusi, Ind. Eng. Chem. Fundam., 11, 123 (1972).

17. Tada, K., S. Shikagawa, and I Nakamori, a paper presented at the 37th annual meeting of the Society of Chemical Engineers, Japan, Nagoya, Japan, April (1972).

18. Gupta, S. P. and R. A. Greenkown, a paper presented at the 72nd National Meeting of the AIChE, St. Louis, MO., May 21-24 (1972).

19. Liu, S. L. and N. R. Amundson, Ind. Eng. Chem. Fundamentals, 2, 183 (1963).

20. Paris, J. R. and W. F. Stevens, Can. J. Chem. Eng., 48, 100 (1970).

21. Feick, J. and D. Quon, Can. J. Chem. Eng., 48, 205 (1970).

22. Lapidus, L., "Digital Computation for Chemical Engineering," McGraw-Hill Co., New York (1962).

23. Smith, G. D., "Numerical Solution of Partial Differential Equations," Oxford University Press, Oxford (1965).

4. GASEOUS POLLUTANT REMOVAL BY A SINGLE BED CYCLIC ADSORBER WITH SYNCHRONOUS THERMAL CONTACT

The adsorption process has been employed mostly in the separation of fluids and solvent recovery (Treybal, 1968). The adsorption process has also been increasingly employed for pollutant removal from air (Faulkner et al. 1973). An adsorption unit usually consists of one, two or more fixed-bed adsorbers (Danielson, 1967; Stern, 1968). To remove the pollutant (the adsorbate), a pollutant laden air stream can be passed through an adsorbent-packed bed or beds wherein the pollutant is concentrated. The adsorption process is continued until the effluent stream from the bed reaches the threshold or maximum allowable concentration. At this point the concentrated pollutant must be disposed. The disposal of the pollutant may be effected in any of the following ways: (1) The adsorbent along with the pollutant is discarded. (2) The pollutant is desorbed and either recovered, if it contains valuable components, or discarded. (3) The pollutant is oxidized on the adsorbent surface and removed.

Among the methods of disposing the concentrated pollutant, the on-site (or in-system) desorption which gives rise to a cyclic operation appears to be most practical, because this method has the following advantages over other methods: (1) No handling of solids is needed during operation. (2) No replacement of the adsorber is necessary. (3) The adsorption-desorption cycles are repeated continuously. The last point is of particular importance for those situations where the pollutant is generated all the time. To achieve a continuous cyclic operation, usually two or more adsorber beds are used (Stern, 1968; Mattia, 1972). However, as is shown in this paper, a single bed adsorber can also handle the continuous pollutant flow effectively. The primary aim of the present study is to show the feasibility of such a single bed adsorber-desorber system (or simply single bed adsorber system) and understand its performance through computer

simulation. Such a compact system can be installed in restaurants, laundries, foundries, laboratories, painting rooms, workshops, mines, etc. It can also find application in space ships and submarines due to its compact character.

Cyclic adsorption-desorption processes for fluid seperation have been studied by several investigators. Wilhelm et al. (1966, 1968) and Sweed and Wilhelm (1969) first introduced the concept of parametric pumping. Parametric pumping is a cyclic separation process in which two synchronous actions --- a periodic temperature variation and an alternating fluid flow --- are imposed on a bed of adsorbent. The alternating fluid flow through the adsorber is coupled with cycling of temperature levels, thus causing a build-up of separation from cycle to cycle. Such a system is a closed system in which the fluid mixture flows between two reservoirs at two opposite ends of the adsorber. There is neither feed introduced nor product withdrawn during the cycles until the separation is complete. This is equivalent to a batch process. Gregory and Sweed (1970, 1972) and Chen et al. (1971, 1972) later modified it by continually introducing the feed and withdrawing the product during portions of a cycle. As for the mathematical model of the adsorption process, Pigford et al. (1969) assumed an equilibrium theory while Gupta and Sweed (1972) presented a more realistic non-equilibrium theory. Recently, Kowler and Kadlec (1972) considered the separation of a gaseous mixture in a fixed bed adsorber by cyclically regulating the pressure gradients in the bed. For the pollution control oriented adsorption system presented here, some operational schemes based on a concept similar to the parametric pumping with thermal contact are incorporated. These schemes are to be arranged so that the continuous flow of the pollutant laden air stream is possible.

The desorbed pollutant may be scrubbed by water or it can be burned and disposed. Since water scrubbing usually requires a large scrubbing tower and may cause water pollution (Faulkner, 1973), it is not desirable for the compact system under consideration. In the present system the desorbed pollutant is burned into harmless gases and thus an incinerator is included in the system.

In the following, the operational schemes of the system under consideration are first described. The mathematical model for the adsorber is then formulated and the effects of some significant parameters on the performance of the system are investigated by computer simulations.

4.1. OPERATIONAL SCHEMES

Two operational schemes are proposed here. One uses fresh air for desorption and the other uses exhaust gas, as shown in Figures 1 and 2, respectively. The adsorber is packed with a bed of activated carbon. Activated carbon is used as adsorbent because it is very effective in adsorbing different organic molecules, even from a humid gas stream (Stern, 1968; Hassler, 1967). The adsorber is embeded with a coiled tube for cooling or heating purposes (Alternatively, the adsorber can be embeded with parallel tubes in a manner similar to a shell and tube heat exchanger). It is assumed that the temperature in the bed can be kept uniform by means of the tube (or tubes). The jacketed incinerator is used to burn the pollutant during the desorption period and it also serves as a heat exchanger.

At the beginning of a cycle, the adsorber bed is cooled to a desirable temperature by flowing a cool fresh air stream or cold water through the coiled tube as shown in Figures 1 and 2. While the bed is kept cool, the pollutant laden air stream (henceforth called feed) flows through the bed from top to bottom. Initially, the adsorbent is relatively clean so that the pollutant is almost completely adsorbed. Consequently, the effluent air stream is virtually free of the pollutant and can be ejected to the atmosphere. As adsorption continues, the adsorbent becomes increasingly saturated and the pollutant concentration in the effluent stream increases gradually. When the effluent concentration reaches the maximum allowable concentration, the adsorption process is interrupted and the system is switched to the desorption phase. A plot of the effluent pollutant concentration versus time is called a breakthrough curve and is illustrated in Figure 3 where c_f is the feed concentration and C_{max} is the maximum allowable concentration. Thus, when the effluent concentration

Scheme I

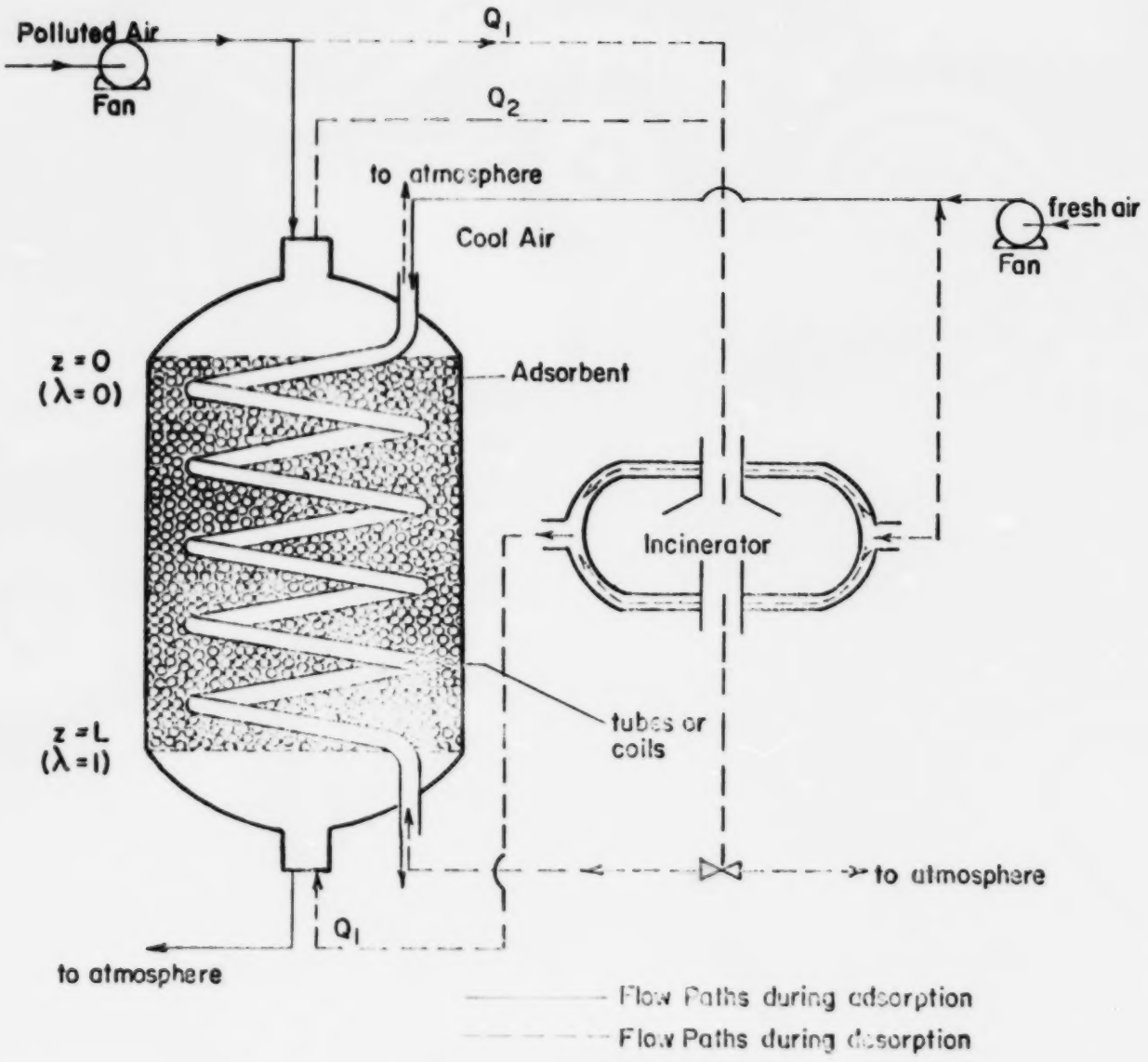

Fig. 1. A single adsorber system using fresh air for desorption.

Scheme II

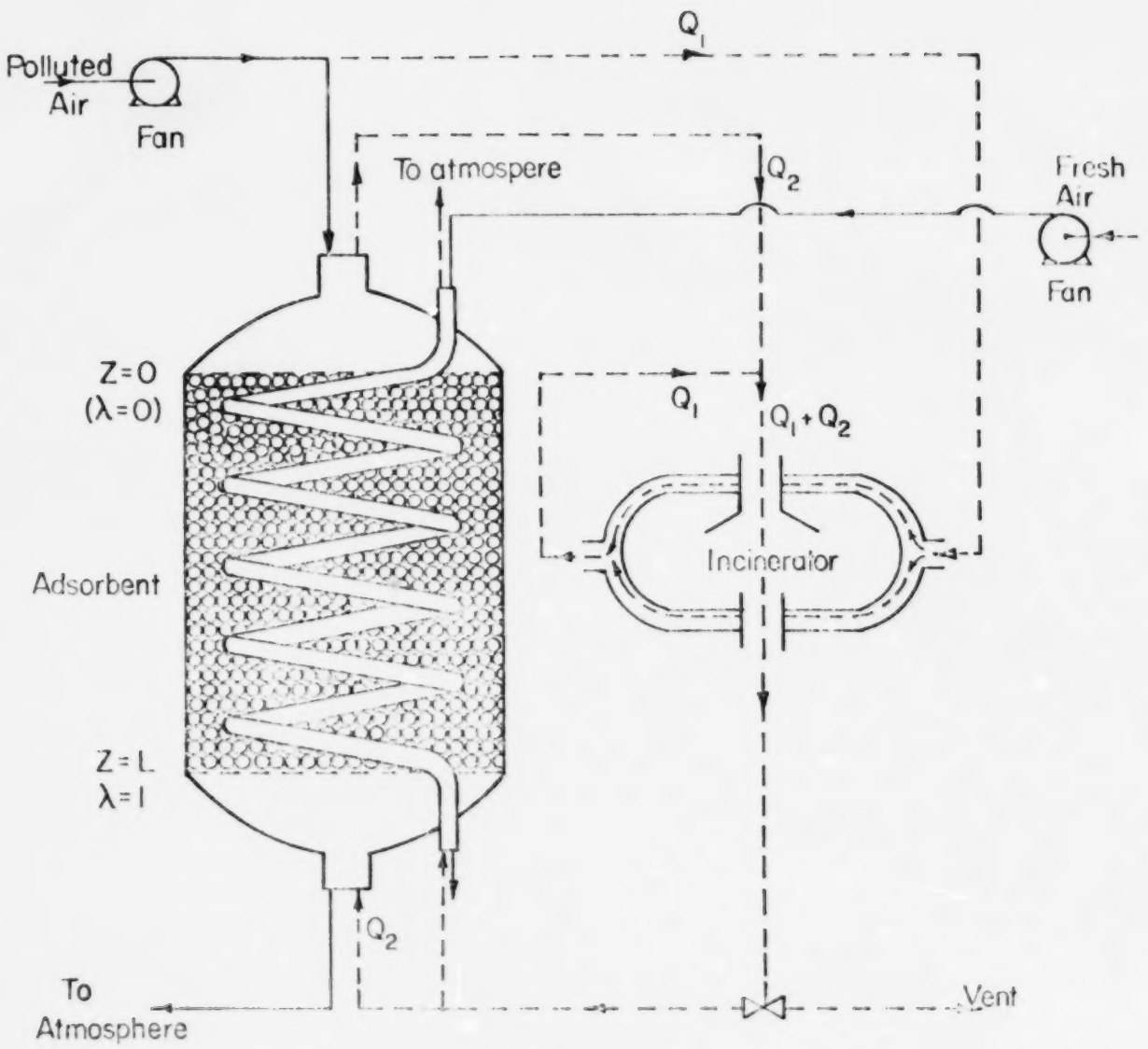

Fig. 2. A single adsorber system using exausted air for desorption.

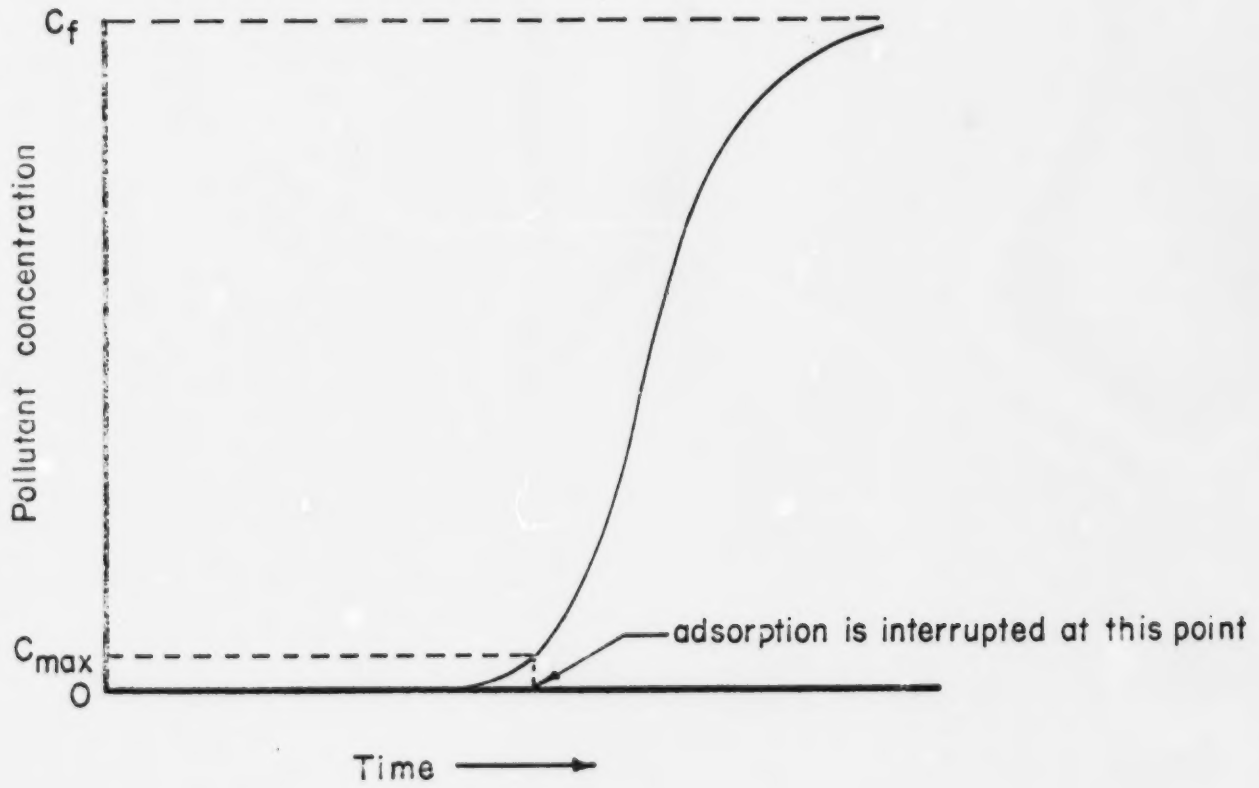

Fig.3. Schematic of a typical breakthrough curve.

reaches C_{max}, the feed is diverted to the incinerator where it is burned together with the desorbed pollutant. It is assumed that the capacity of the incinerator is large enough so that the pollutant can be burned almost completley. Thus the exhaust from the incinerator is free of the pollutant.

The desorption process can be effected by two different schemes. These are distinguished as scheme I in Figure 1 and scheme II in Figure 2. In scheme I a portion of the exhaust gas from the incinerator is allowed to flow through the coiled tube to raise the bed temperature. At the same time, a fresh air stream flows through the jacket of the incinerator. The heated fresh air stream then flows upward through the bed to desorb the pollutant. The desorbed pollutant stream combines with the original pollutant laden stream before entering the incinerator. The desorption process is stopped when the bed has been cleaned to a certain level (This point will be detailed later). This completes one adsorption-desorption cycle. Thus, within a cycle, the direction of flow is changed synchronously with the change of bed temperature.

Scheme II is a modification of scheme I. It differs from scheme I in that it does not require an additional fresh air stream for desorption. The exhaust gas stream from the incinerator is divided into two streams; one is used to heat the adsorber through the coiled tube and the other to desorb the pollutant. Since it is assumed that the exhaust gas is essentially free of pollutant, it can be considered as an inert gas and thus has the same desorbing property as fresh air. Note that the feed stream is heated in the incinerator jacket before it combines with the desorbed polluted stream. Thus, the heat loss due to mixing is reduced.

In comparing the two schemes described above, it appears that Scheme II is more advantageous than scheme I because no additional air stream is

required and heat loss due to mixing is reduced. Furthermore, in scheme II, an inert gas is used for desorption. This can prevent the activated carbon in the bed from being oxidized. Scheme II, however, does have some disadvantages. The stream entering the incinerator is diluted due to mixing of the desorbed stream with the feed stream (see Figure 2), and this dilution may require excessive thermal energy for incineration of the pollutant. Moreover, if the exhaust gas from the incinerator contains a substantial amount of particulates, the exhaust gas stream should pass a filter before entering the adsorber.

4.2. MATHEMATICAL MODEL OF THE ADSORBER

The assumptions made in deriving the performance equations of the single adsorber system under consideration are:

(a) The adsorption process takes place isothermally at a lower temperature and the desorption process takes place isothermally at a higher temperature.

(b) External mass transfer is the rate controlling step. The model of mass transfer based on this assumption is called the film model.

(c) Parameters such as mass transfer coefficient, porosity of bed, adsorbent density, specific surface area of adsorbent, etc.. do not change with respect ot operating conditions.

(d) No dispersion of the gaseous components occurs in the entrance and exit sections adjacent to the bed, although the existence of dispersion within the bed is not neglected.

Under these assumptions, the following differential equations can be written by taking mass balances on the adsorbate and the adsorbent.

$$H_g \frac{\partial c}{\partial t} = \varepsilon \rho_g D \frac{\partial^2 c}{\partial z^2} \mp G \frac{\partial c}{\partial z} - k_e a \rho_g (c - c^*) \qquad (1)$$

$$H_s \frac{\partial q}{\partial t} = k_e a \rho_g (c - c^*) \qquad (2)$$

The ambiguous sign in equation (1) accounts for the direction of the gaseous flow. The positive direction is that from top to bottom. In other words, the positive direction in the bed is always measured from the top. Thus, the "-" should be used during adsorption while the "+" should be used during desorption. In equations (1) and (2), c^* is the gas phase equilibrium concentration which is related to q by a Langmuir type isotherm

$$q = \frac{q_m \; b \; c^*}{1 + b \; c^*} \tag{3}$$

where q_m is the amount of adsorbate on unit mass of adsorbent when the adsorbent is fully covered by a monolayer of the adsorbate. The constant b is determined from (Brunauer, 1943)

$$b = \frac{A_1 \exp(A_2/T)}{T^{\frac{1}{2}}} \tag{4}$$

where A_1 and A_2 are constants and T is the temperature of the adsorber bed.

Let the over-all time or period of each cycle be t_c, the adsorption time t_a, and the desorption time t_d. It is assumed that the switching from adsorption to desorption is instantaneous so that $t_c = t_a + t_d$. Because of the cyclic steady state nature of the operation, the initial conditions of the adsorption process are those at the end of the desorption and vice versa. These conditions along with the appropriate boundary conditions for equations (1) and (2) can be expressed mathematically as shown below, noting that the directions of flow are opposite to each other during the adsorption and desorption processes.

During adsorption

$$c\,(0,z) = c(t_c^-,\; L - z) \tag{5}$$

$$q\,(0,z) = q(t_c^-,\; L - z) \tag{6}$$

$$\left.\begin{aligned} c\,(t,0) &= c_f + \frac{\varepsilon \rho_g \mathcal{D}}{G} \frac{\partial c(t,\,0)}{\partial z} \qquad (7) \\ \frac{\partial c\,(t,\,L)}{\partial z} &= 0 \qquad (8) \end{aligned}\right\}, \; 0 \leq t \leq t_a^-$$

During desorption

$$c(t_a^+, z) = c(t_a^-, L - z) \tag{9}$$

$$q(t_a^+, z) = q(t_a^-, L - z) \tag{10}$$

$$\left.\begin{aligned} c\ (t, L) &= c^d - \frac{\varepsilon\ \rho_g D}{G}\ \frac{\partial c(t,L)}{\partial z} \qquad (11) \\ \frac{\partial c}{\partial z}\ (t, 0) &= 0 \qquad (12) \end{aligned}\right\}\ ,\ t_a^+ \leq t \leq t_c^-$$

In the above equations c^d is the inlet concentration of the pollutant in the desorbing air stream. For either scheme, c^d is zero since the desorbing stream contains no pollutant. t_a^- indicates the end of the adsorption period, t_a^+, the beginning of the desorption period, and t_c^- the end of the desorption period. The temperature, T, in equation (4) takes on T_a for adsorption and T_d for desorption.

Equations (1) through (12) can be rewritten in dimensionless forms by introducing the following dimensionless quantities.

$$X = \frac{c}{c_f}$$

$$Y = \frac{q}{q_m}$$

$$\lambda = \frac{z}{L}$$

$$\tau = \frac{tG}{L\ H_g}$$

$$Pe = \frac{GL}{\varepsilon\ \rho_g\ D}$$

$$K_e = \frac{k_e a \rho_g L}{G}$$

$$\alpha = \frac{H_g c_f}{H_s q_m}$$

$$B = b c_f$$

The resulting govering equations are

$$\frac{\partial X}{\partial \lambda} = \frac{1}{Pe} \frac{\partial^2 X}{\partial \lambda^2} + \frac{\partial X}{\partial \lambda} - K_e (X - X^*) \tag{13}$$

$$\frac{\partial Y}{\partial \tau} = K_e (X - X^*) \tag{14}$$

where X^* is determined from the equilibrium condition

$$Y = \frac{BX^*}{1 + BX^*} \tag{15}$$

The corresponding dimensionless initial and boundary conditions are, during adsorption

$$X(0, \lambda) = X(\tau_c^-, 1 - \lambda) \tag{16}$$

$$Y(0, \lambda) = Y(\tau_c^-, 1 - \lambda) \tag{17}$$

$$X(\tau, 0) = 1 + \frac{1}{Pe} \frac{\partial X(\tau,0)}{\partial \lambda} \tag{18}$$

$$\frac{\partial X(\tau,1)}{\partial \lambda} = 0 \tag{19}$$

$$0 \leq \tau \leq \tau_a^-$$

during desorption

$$X(\tau_a^+, \lambda) = X(\tau_a^-, 1 - \lambda) \tag{20}$$

$$Y(\tau_a^+, \lambda) = Y(\tau_a^-, 1 - \lambda) \tag{21}$$

$$\left.\begin{aligned} X(\tau, 1) &= -\frac{1}{Pe}\,\frac{\partial X(\tau,1)}{\partial \lambda} \qquad (22) \\ \frac{\partial X(\tau,0)}{\partial \lambda} &= 0 \qquad (23) \end{aligned}\right\}, \tau_a^+ \leq \tau \leq \tau_c^-$$

Equations (13) through (15) together with equations (16) through (23) cannot be solved analytically because of the nonlinearity appearing in equation (15). They, can be solved however, by the finite difference method (Ames, 1969). It should be noted that the solutions for schemes I and II are identical although there is a practical difference in operation between the two schemes as described previously.

4.3. RESULTS OF SIMULATION AND DISCUSSION

The performance of the adsorber system under consideration is examined with respect to significant parameters such as:

(1) pollutant concentration in the feed,

(2) maximum allowable concentration,

(3) adsorption temperature,

(4) desorption temperature,

(5) linear velocity of the gas flow,

(6) residual pollutant loading at the end of desorption, and

(7) extent of the axial dispersion characterized by the Peclet number.

The first parameter depends on the content of a pollution source. The second parameter is related to human tolerance toward the pollutant and is regulated usually by emission standards. The other parameters are subject to a desinger's choice. Thus it is desirable to examine effects of each parameter on the system performance. As a basis for comparison, the results of simulation for a set of nominal values of the parameters are first presented and discussed. The effects of each parameter are analyzed subsequently.

The numerical values of the nominal conditions are listed in Table 1. Additional constants employed in the simulation are listed in Table 2. Under these conditions, the dimensionless quantities K_e and α are,

for adsorption, $K_e = 45.0$

$$\alpha = 1.046 \times 10^{-6}$$

for desorption, $K_e = 37.46$

$$\alpha = 8.71 \times 10^{-7}$$

Table 1. Numerical Values of Nominal Conditions

(1)	C_f, feed concentration	500 ppm
(2)	C_{max}, maximum allowable concentration	25 ppm
(3)	T_a, adsorption temperature	25°C
(4)	T_d, desorption temperature	70°C
(5)	P, pressure in the adsorber	1 atm
(6)	u, superficial linear velocity of gaseous flow	40 cm/sec.
(7)	ß, residual pollutant loading at the end of desorption	5%
(8)	Pe, Peclet number	200

Table 2. Additional Constants Employed in the Simulation

$a = 15\ cm^2/cm^3$

$A_1 = 0.2312 \times 10^{-3}\ (°K)^{\frac{1}{2}}$

$A_2 = 0.44076 \times 10^4\ °K$

$D_a = 30\ cm.$

$d_p = 0.4\ cm.$

$k_e = 3\ cm/sec.$

$L = 40\ cm.$

$q_m = 0.5\ g/g$

$\epsilon = 0.4$

$\rho_s = 0.75\ g/cm^3$

In this study, the direction of flow during desorption is opposite to that during adsorption. This is due to the fact that at the end of adsorption, a pollutant concentration gradient exists in the bed where the upper portion is almost saturated while the lower portion is relatively clean. If desorption were conducted in the same direction, some of the pollutant which has been desorbed from the upper portion would be readsorbed in the lower portion, thereby hindering the desorption process. If desorption were conducted in the opposite direction this phenomenon would not occur.

Figures 4 and 5 show the distributions of the pollutant concentrations in the gas and solid phases, respectively, during the adsorption period. It can be seen that at the early stage of adsorption, only a narrow zone near the top end is contaminated. As the period of time increases, the pollutant concentrations in both the gas and solid phases increase at every point. Of particular interest is the increase in the gas phase at the exit ($\lambda = 1$) as shown in Figure 6. The effluent concentration is essentially free of pollutant for approximately 26 minutes, after which it increases very sharply. As soon as the maximum allowable concentration (in this case, 25 ppm) is reached, the adsorption operation is interrupted. The amount of pollutant loaded on the adsorbent can be obtained by integrating

$$Q_l = \rho_s (1 - \varepsilon) q_m AL \int_0^1 Y_{fA} d\lambda \tag{24}$$

where Y_{fA} is the solid phase pollutant concentration profile at the termination of adsorption. Note that the quantity

$$\int_0^1 Y_{fA} \, d\lambda$$

is represented by the shaded area in Figure 5.

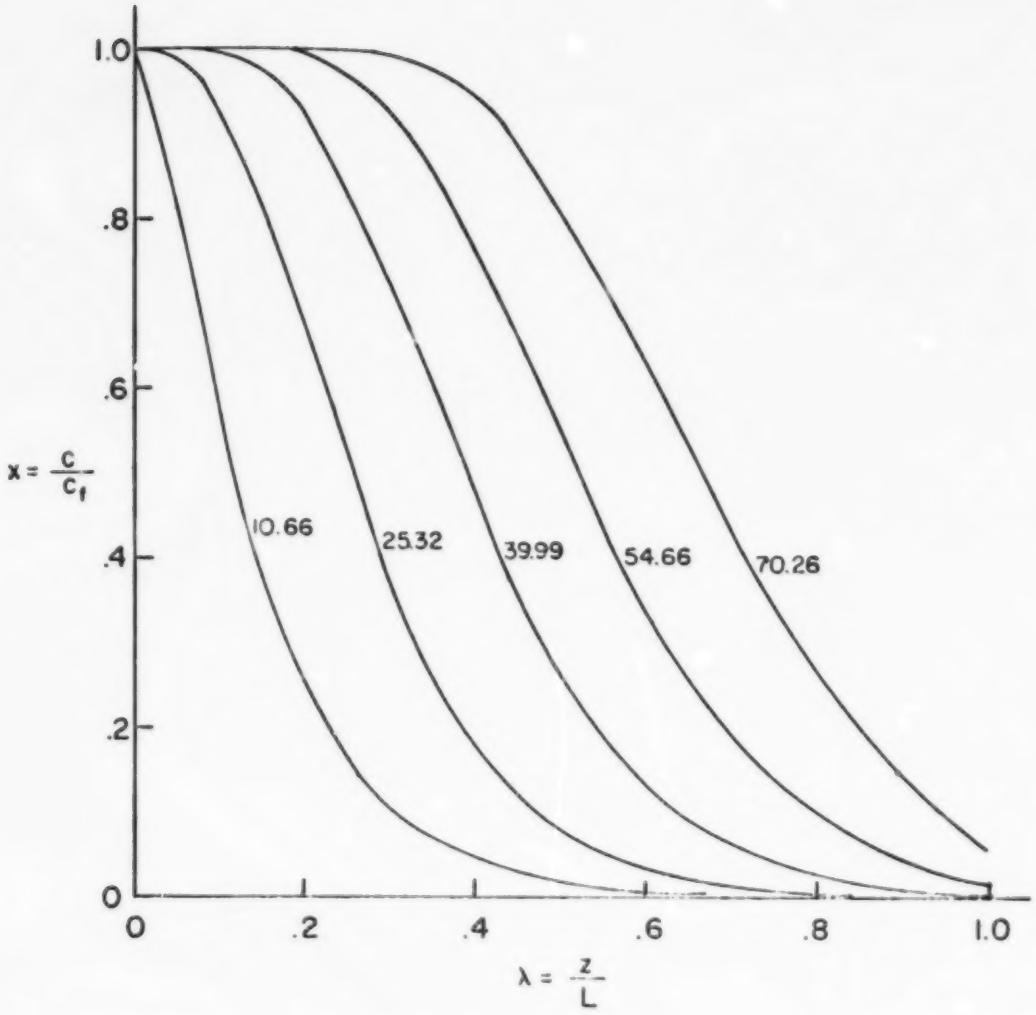

Fig. 4 Gas phase pollutant concentration during adsorption period (Nominal conditions; parameter: time, min.).

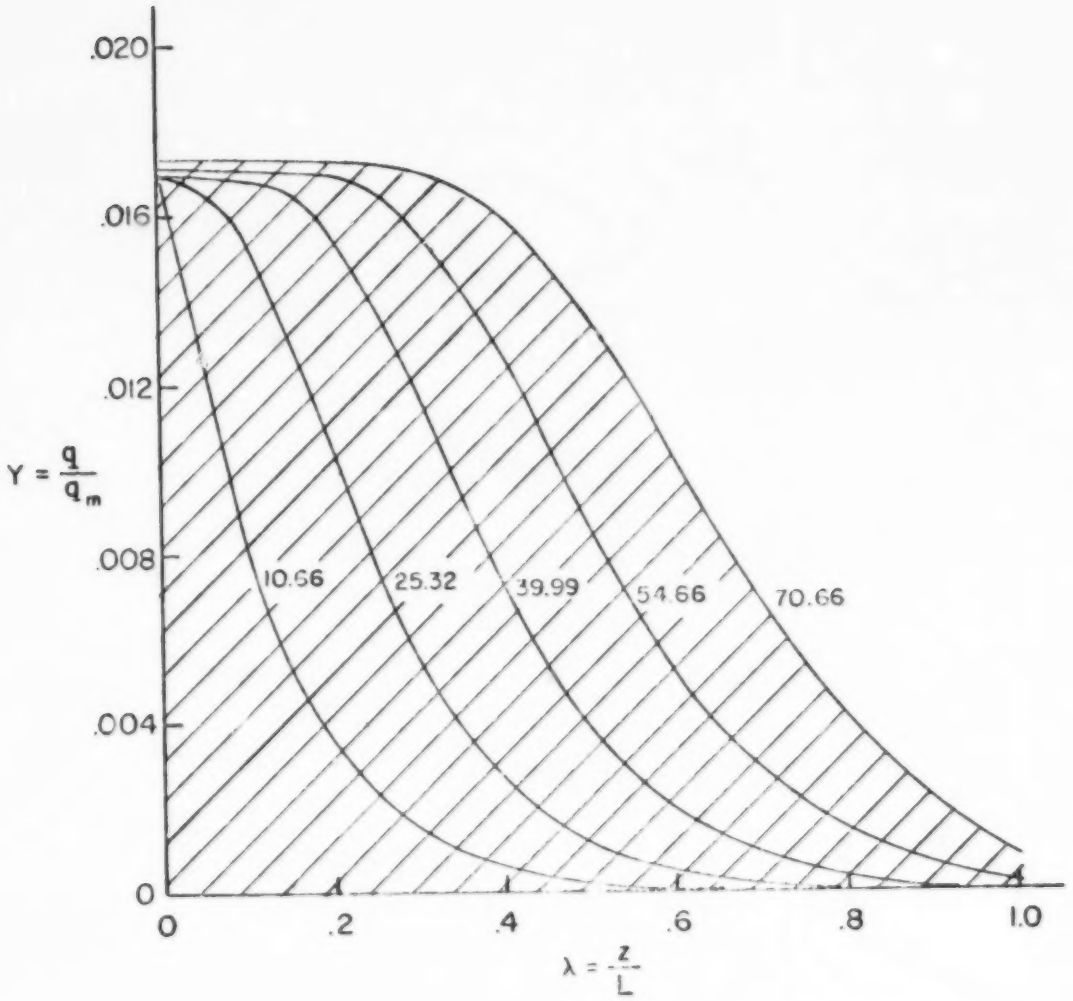

Fig. 5 Solid phase pollutant concentration during adsorption period (Nominal conditions; parameter : time, min.).

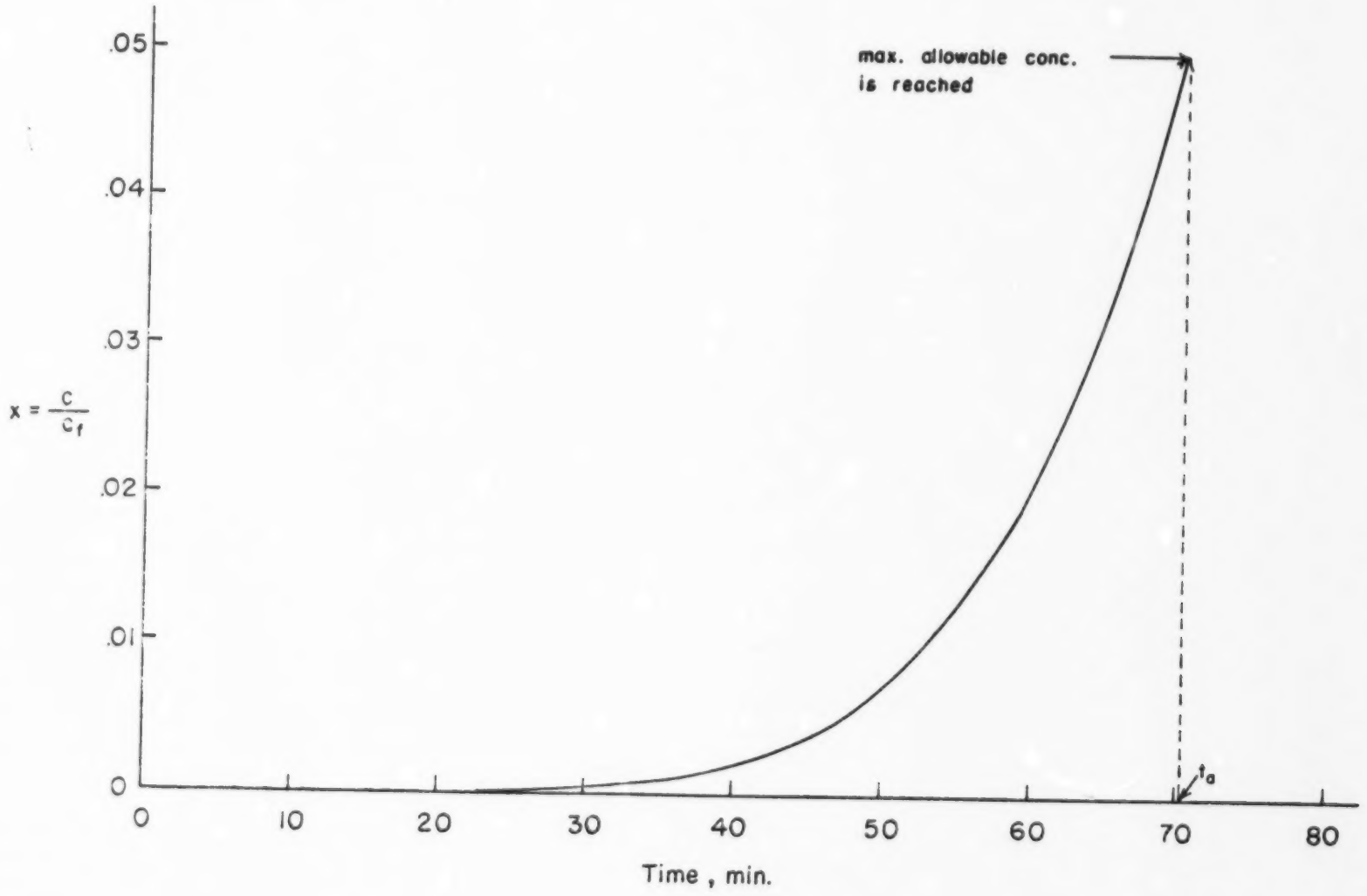

Fig. 6 Effluent pollutant concentration during adsorption period (Nominal conditions).

As soon as adsorption is terminated, desorption is initiated. During the desorption operation, the pollutant concentrations in the gas and solid phases decrease as shown in Figures 7 and 8, respectively. Since the desorbing air stream flows upward, the pollutant is desorbed faster in the lower part (larger λ) than in the upper part (smaller λ). Desorption is terminated when the residual pollutant loading on the adsorbent is at a certain fraction (in the nominal case, 5%) of the original loading, i.e., Q_1. The amount of the residual pollutant on the adsorbent can be obtained as

$$Q_2 = \rho_s (1 - \varepsilon) q_m AL \int_0^1 Y_{fD} \, d\lambda \tag{25}$$

where Y_{fD} is the solid phase pollutant concentration profile at the end of desorption. As before, the quantity

$$\int_0^1 Y_{fD} \, d\lambda$$

is represented by the shaded area in Figure 8.

The capacity of adsorption per cycle is defined as the difference between the original loading and the residual loading. Let the capacity be denoted by ΔQ. Then

$$\Delta Q = Q_1 - Q_2 \tag{26}$$

This quantity divided by the time of a cycle gives the pollutant removal rate of the adsorber. The adsorption time or period, desorption time, capacity per cycle, and removal rate of the adsorber along with the values of the parameters are tabulated in Table 3. These values for the nominal

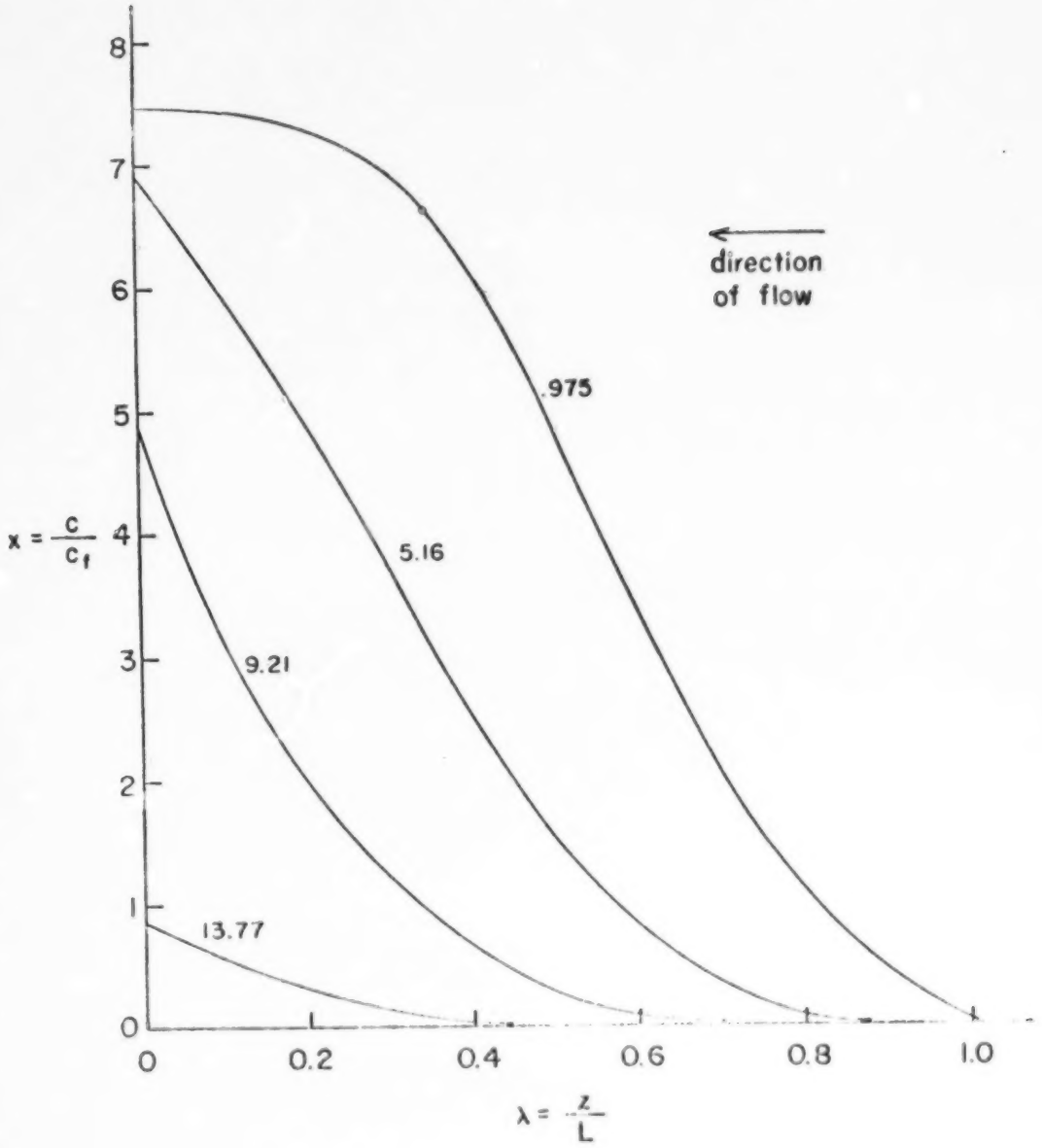

Fig. 7 Gas phase pollutant concentration during desorption period (Nominal conditions, parameters : time, min.).

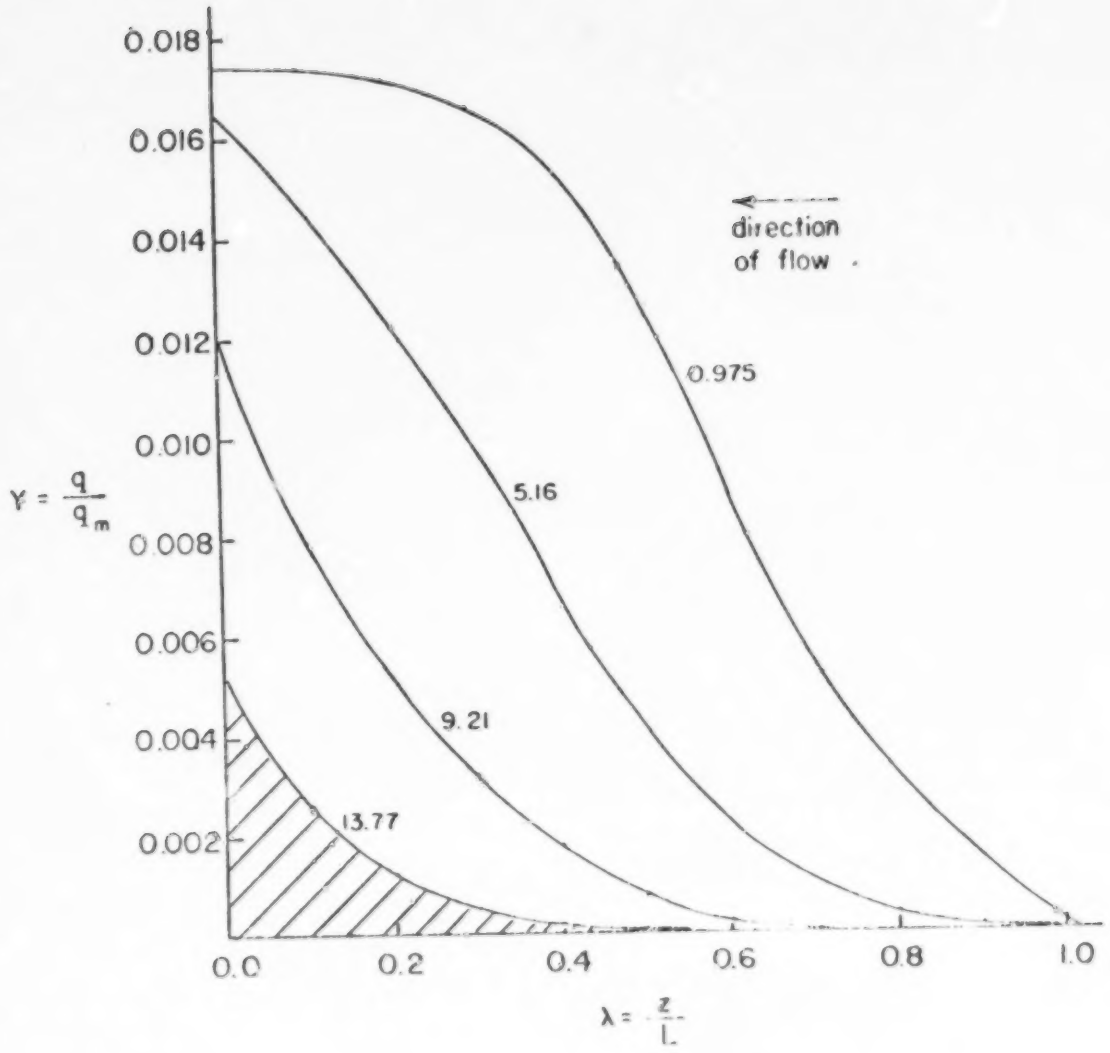

Fig. 8 Solid phase pollutant concentration during desorption period (Nominal conditions, parameters : time, min.).

Table 3. Effects of Various Parameter on Adsorber Performance

parameters									adsorption time, min.	desorption time, min.	fraction of desorption operation	capacity of adsorption g/cycle	removal rate of adsorber g/min.
No.	C_f ppm	C_{max} ppm	T_a °C	T_d °C	P atm	u cm/s	β %	Pe No.					
1	500	25	25	70	1	40	5	200	70.3	13.8	0.164	68.9	0.820
2	250	25	25	70	1	40	5	200	79.5	14.6	0.155	38.5	0.409
3	1000	25	25	70	1	40	5	200	62.5	13.0	0.172	123.3	1.633
4	500	10	25	70	1	40	5	200	60.5	12.7	0.173	59.9	0.818
5	500	50	25	70	1	40	5	200	79.3	14.6	0.155	76.8	0.818
6	500	25	20	70	1	40	5	200	89.4	13.6	0.132	89.2	0.866
7	500	25	30	70	1	40	5	200	55.7	14.0	0.201	53.7	0.770
8	500	25	25	60	1	40	5	200	70.3	20.5	0.226	69.0	0.760
9	500	25	25	80	1	40	5	200	70.3	9.5	0.119	68.9	0.863
10	500	25	25	70	0.5	40	5	200	140.7	27.2	0.162	68.9	0.410
11	500	25	25	70	2	40	5	200	35.2	6.8	0.162	68.9	1.640
12	500	25	25	70	1	30	5	200	98.3	18.1	0.155	72.3	0.621
13	500	25	25	70	1	50	5	200	53.7	11.2	0.173	65.8	1.014
14	500	25	25	70	1	40	1	200	75.1	17.6	0.190	73.9	0.797
15	500	25	25	70	1	40	10	200	63.9	11.7	0.155	62.9	0.832
16	500	25	25	70	1	40	5	100	65.2	13.2	0.168	64.3	0.820
17	500	25	25	70	1	40	5	∞	83.6	19.8	0.191	78.9	0.763

case are contained in the first row. Starting from the second row, one parameter each is varied from the nominal values. The values which deviate from the nominal values are encircled.

The effects of the various parameters on the adsorber performance are discussed in what follows.

(1). Feed Concentration

The results in Table 3 show that the removal rate of the adsorber is almost proportional to the feed concentration. However, the cycle time decreases with increasing feed concentration but the fraction of time for the desorption operation increases with increasing feed concentration. Hence a higher feed concentration needs more frequent desorption. Furthermore, a higher feed concentration is usually achieved by applying pressure. Higher pressure in the adsorber not only increases the power cost but also adds construction cost. Therefore, a higher feed concentration has no advantage for the cyclic operation.

The mathematical model is simulated for two different feed concentrations, one lower and one higher than the nominal values, keeping all other parameters unchanged. The results are presented in row 2 and row 3, respectively, of Table 3. It is obvious that if the feed concentration is lower, the pollutant removal rate is lower, and vice versa.

(2). Maximum Allowable Concentration

As mentioned previously, the maximum allowable concentration is usually regulated by local emission standards. If a stricter emission standard is imposed on the system, the maximun allowable concentration, C_{max} should be lowered. Conversely, if the emission standard is slackened, C_{max} can be increased.

The pollutant removal rates for different values of C_{max} are almost identical. However, the cycle time increases with increasing C_{max}, but the fraction of time for desorption operation decreases with increasing C_{max}. The results from the effect of this parameter are given in rows 4 and 5 of Table 3. It is interesting to note that the pollutant removal rates for different values of C_{max} are almost identical although the adsorption time, desorption time, and adsorption capacities vary significantly.

(3). Adsorption Temperature

At the temperature of 20°, 25°, and 30° C, the adsorption times are 89.4, 70.3, and 55.7 minutes, respectively. These results indicate that the adsorption process is very sensitive to the adsorption temperature. The cycle time increases with decrease in adsorption temperature but the fraction of time for the desorption operation decreases with decreasing adsorption temperature. Moreover, the lower the adsorption temperature the higher the removal rate of adsorber. Therefore, low temperature favors pollutant adsorption.

At the nominal temperature, 25°C, the adsorption time is 70.3 minutes. At 20°C, the adsorption time is 89.4 minutes, an increase of 27%. On the other hand, if the adsorption temperature is 30°C, the adsorption time is reduced to 55.7 minutes, a reduction of 21%. These results indicate that the adsorption process is very sensitive to the adsorption temperature. A similar observation can be drawn by comparing the pollutant removal rate at different temperatures (see rows 1, 6, and 7 of Table 3).

(4). Desorption Temperature

It can be seen from Table 3 that the desorption process is also very sensitive to temperature. At the temperature of 80, 70, 60°C, the

desorption times are found to be 9.5, 13.8, and 20.5 minutes, respectively. Logically, the desorption temperature should be as high as possible. However, the cost of thermal energy and the thermal stability of the bed constrain the maximum desorption temperature.

(5). Pressure

The results reveal that the adsorption time and desorption time are almost inversely proportional to the pressure. However, the fraction of time for the desorption operation is essentially independent of the pressure in the range of operation. The results also show that the capacity per cycle does not change with the pressure. Therefore, the removal rate of the adsorber is proportional to the pressure. The operating pressure depends on the purpose and situation of operation. From the viewpoint of energy cost, the adsorber should be operated under the atmospheric pressure except in a space ship or submarine where a lower or higher pressure prevails naturally.

(6). Superficial Velocity of Gaseous Flow

The value of the linear velocity of gaseous flow given in Table 1 is selected at the adsorption temperature. If the same mass flow rate of air is maintained, the linear velocity during the desorption period is higher than that during the adsorption period because the temperature during the former is higher than that during the latter.

The recommended linear velocities for adsorption fall between 24 and 55 cm/sec. (Treybal, 1968). The nominal value is chosen to be 40 cm/sec.. As shown in Table 3, the adsorption time is relatively longer but the desorption time is only slightly prolonged at a lower velocity. On the other hand, the adsorption time is shortened much more than the

desorption time at a higher velocity. Most significantly, the pollutant removal rate is much higher at the higher velocity. A desirable situation is one where the linear velocity is low enough so that the energy for transporting the gas is small and yet is high enough so that the high removal rate is maintained.

(7). Residual Pollutant Loading at the End of Desorption

Lowering of the residual pollutant at the end of desorption prolongs the desorption time. It is also prolongs the adsorption time and increases the adsorption capacity. However, in terms of the pollutant removal rate, this does not yield a higher value. As the results in Table 3 indicate, the residual pollutant load should remain reasonably high in order to maintain a high pollutant removal rate.

(8). Extent of Dispersion

Since

$$Pe = \frac{GL}{\varepsilon \rho_g D} \quad \text{and} \quad G = u\rho_g$$

the Peclet number can be rewritten as

$$Pe = \frac{uL}{D\varepsilon}$$

For the operating conditions under consideration, the Schmidt number is approximately unity (see Appendix) and the Reynolds number is in the neighborhood of 100. Under these conditions, the dimensionless group $D\varepsilon/ud_p$ is approximately equal to 0.5 (Levenspiel, 1962) where d_p is the adsorbent particle diameter. Therefore,

$$Pe = \frac{uL}{D\varepsilon} = \frac{ud_p}{D\varepsilon} \cdot \frac{L}{d_p} \doteq 2\frac{L}{d_p}$$

The Peclet number can be perceived as depending only on the adsorber length (bed depth) and the adsorbent particle diameter. The adsorption and desorption times calculated using different Peclet numbers are shown in Table 3. It can be seen that the higher the Peclet number or the less the mixing, the longer the adsorption time. Thus, a higher Peclet number is favorable because it requires less frequent desorption. However, a large Peclet number must be achieved by using finer particles and/or a longer adsorber. This gives rise to a higher pressure drop. Furthermore, a large Peclet number does not yield a higher removal rate.

NOMENCLATURE

A = cross-sectional area of the adsorber, cm^2.

a = available external surface area per unit volume of bed, cm^2/cm^3.

A_1 = constant, $(^oK)^{\frac{1}{2}}$.

A_2 = constant, ^oK.

b = adsorption coefficient expressed in the Langmuir isotherm equation.

B = adsorption coefficient expressed in equation (15).

c = adsorbate concentration in gas phase, g of adsorbate/g of adsorbate free gas.

c^* = equilbrium concentration, g of adsorbate/g of adsorbate free gas.

c_f = pollutant concentration, g of adsorbate/g of adsorbate free gas.

c_{max} = maximum allowable concentration, g of adsorbate/g of adsorbate free gas.

D = axial dispersion coefficient for mass transfer, cm^2/sec.

D_a = diameter of the adsorber, cm.

d_p = adsorbent particle diameter, cm.

G = mass flow rate of fluid per unit cross-sectional area, g of gas/sec-cm^2.

H_g = gas phase hold-up, i.e., mass of gas per unit volume of bed, g of gas/cm^3 of bed.

H_s = solid phase hood-up, i.e., mass of adsorbent per unit volume of bed, g of adsorbent/cm^3 of bed.

k_e = external mass transfer coefficient based on external surface of particle and concentration driving force, cm/sec.

K_e = dimensionless mass transfer coefficients, $\frac{k_e a \rho_g L}{G}$

L = depth of adsorber bed, cm.

P = pressure in the adsorber, atm.

Pe = Peclet number, $\frac{GL}{\varepsilon \rho_g D}$

Q_1 = amount of adsorbate loaded on the adsorbent at the end of adsorption, g.

Q_2 = amount of adsorbate remaining on the adsorbent at the end of desorption, g.

ΔQ = $Q_1 - Q_2$, capacity of adsorption, g.

q = amount of adsorbate adsorbed per unit mass of adsorbent, g of adsorbate/g of adsorbent.

q_m = amount of adsorbate adsorbed per unit mass of adsorbent, when the adsorbent is fully covered by a monolayer, g of adsorbate/g of adsorbent.

t = time, sec.

T = temperature, ^{o}K.

T_a = adsorption temperature, ^{o}C.

T_d = desorption temperature, ^{o}C.

u = superfical linear velocity of gaseous flow cm/sec.

X = dimensionless adsorbate concentration in gas phase, $\frac{c}{c_f}$

X^* = dimensionless adsorbate equilibrium concentration in gas phase, $\frac{c^*}{c_f}$

Y = dimensionless adsorbate concentration in solid phase, $\frac{q}{q_m}$

z = axial distance from top of bed, cm.

GREEK LETTERS

α = ratio of adsorbate removal capacity in the gas phase to that in in the solid phase in the bed, $\frac{H_g}{H_s}\frac{c_f}{q_m}$

β = residual pollutant loading at the end of desorption

λ = dimensionless axial distance, $\frac{Z}{L}$

ρ_g = density of gas, g/cm^3.

ρ_s = density of adsorbent g/cm^3.

τ = dimensionless time, $\frac{tG}{L H_g}$

ε = void fraction of the bed.

LITERATURE CITED

Ames, W. F., "Numerical Methods for Partial Differential Equations", Barnes & Noble, Inc., New York, 1969.

Brunauer, S., "The Adsorption of Gases and Vapors. Volume I, Physical Adsorption", Princeton University Press, Princeton, N.J., 1943.

Chen, H. T., Hill, F. B., Seperation Sci., 6, 411 (1971)

Chen, H. T., Rak, J. L., Stokes, J. D., Hill, F. B., AIChE J., 18, 356 (1972).

Danielson, J. A., (editor), "Air Pollution Engineering Manual", U.S. Department of HEW, National Center for Air Pollution Control, Cincinnati, Ohio, 1967.

Fan, L. T., Choi, S. K., Institute for Systems Design and Optimization Report No. 41, Kansas State University, Manhattan, Kansas.

Faulkner, W. D., Schuliger, W. G., Urbanic, J. E., presented at 74th AIChE National Meeting, New Orleans, Louisiana, March 12, 1973.

Gregory, R. A., Sweed, H. H., Chem. Eng. Journal, 1, 207 (1970).

Gregory, R. A. Sweed, N. H. ibid, 4, 139 (1972).

Gupta, R., Sweed, N. H., presented at AIChE National Meeting, Minneapolis, Minnesota, August 29, 1972.

Hassler, J. W., "Activated Carbon", Leonard Hill Books, 1967.

Kowler, D. E., Kadlec, R. H., AIChE J. 18, 1207 (1972).

Levenspiel, O., "Chemical Reaction Engineering", p. 275, John Wiley & Sons, New York, 1962.

Mattia, M. M., CEP, 66, 74 (December, 1970).

Pigford, R. L., Baker, B. III, Blum, E. E., I&EC Fundamentals, 8, 144 (1969).

Stern, A. C. (editor), "Air Pollution", Vol. III. Academic Press, 1968.

Sweed, N. H., Wilhelm, R. H., I&EC Fundamentals, 8, 221 (1969).

Treybal, R. E., "Mass-Transfer Operation", 2nd edition McGraw-Hill Book Company, Inc., New York, 1968.

Wilhelm, R. H., Rice, A. W., Bendelius, A. R., I&EC Fundamentals, 5, 141 (1966).

Wilhelm, R. H., Rice, A. W., Rolke, R. W., Sweed, N. H., I&EC Fundamentals, 7, 337 (1968).

5. CONCLUSIONS AND RECOMMENDATIONS

The literature survey and mathematical modeling presented in this report should serve as a convenient reference source for those who are engaged in analysis, design and operation of gas adsorbers for air pollutants.

A computer simulation of the processes taking place in an adsorption bed was carried out, and the combined effect of dispersion and heat of adsorption on the operating characteristics of the adsorption unit was determined. Results of this phase of the study should be useful for advancing the understanding of the behavior of the adsorption unit, for planning laboratory and field experiments, and for interpreting the results of such experiments.

Two new operational schemes for a single column adsorber system were proposed. The performance of such a system was studied by computer simulation. The results of this phase of the study should be useful for design and operation of such an adsorber system. A single adsorber system can be installed easily and operated effectively. Such a system should be especially effective when the limitation of space or weight must be taken into consideration.

Considerable technical information on air pollutant adsorption and several valid mathematical models for packed bed adsorbers for air pollutants are available. While the present study has contributed significantly toward practical applications of such information and mathematical models, much remains to be done. For example, optimization and synthesis studies should be carried out for multiple bed adsorption systems. For this purpose improved mathematical models for regeneration should be developed.

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